

# **Supporting Information**

**for**

## **Low-valent Tungsten Catalyzed Carbonylative Synthesis of Benzoates from Aryl Iodides and Alcohols**

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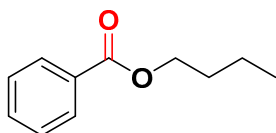
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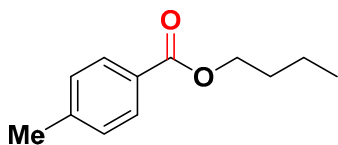
## General information

Melting points were measured using a melting point instrument and are uncorrected.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at TMS (0 ppm) and 77.0 ppm, respectively, and chloroform was used as a solvent with TMS as the internal standard. GC-MS data were obtained using electron ionization. TLC was performed using commercially available 100-400 mesh silica gel plates (GF254). Unless otherwise noted, purchased chemicals were used without further purification.

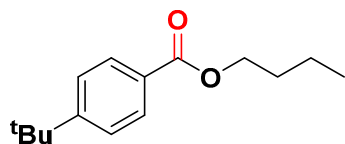
## Characterization data for all products



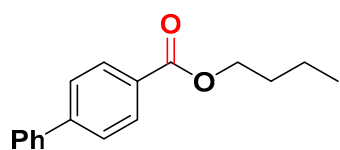
**Butyl benzoate (3a)** [1] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a light yellow oil (82.8 mg, 93%);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.11 (d,  $J$  = 8.0 Hz, 2H), 7.62 (t,  $J$  = 8.0 Hz, 1H), 7.50 (t,  $J$  = 7.6 Hz, 2H), 4.39 (t,  $J$  = 6.6 Hz, 2H), 1.82 (dt,  $J$  = 14.4, 6.8 Hz, 2H), 1.56 (dt,  $J$  = 14.4, 7.2 Hz, 2H), 1.05 (t,  $J$  = 8.0 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  166.7, 132.7, 130.6, 129.5, 128.3, 64.8, 30.8, 19.3, 13.7.



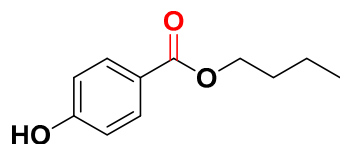
**Butyl 4-methylbenzoate (3b)** [1] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a light yellow oil (87.4 mg, 91%);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.00 (d,  $J$  = 8.0 Hz, 2H), 7.31 (t,  $J$  = 7.8 Hz, 2H), 4.37 (t,  $J$  = 8.0 Hz, 2H), 2.47 (s, 3H), 1.81 (dt,  $J$  = 14.4, 6.8 Hz, 2H), 1.55 (dt,  $J$  = 14.4, 7.2 Hz, 2H), 1.04 (t,  $J$  = 7.4 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  166.8, 143.4, 129.5, 129.0, 127.9, 102.0, 64.6, 30.8, 21.6, 19.3, 13.7.



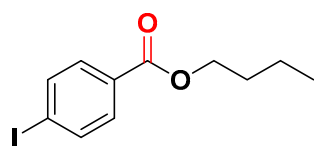
**Butyl 4-(tert-butyl)benzoate (3c)** [2] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a colorless oil (105.4 mg, 90%);  $^1\text{H}$  NMR (400 MHz, Chloroform-d)  $\delta$  8.04 (d,  $J$  = 8.4 Hz, 2H), 7.52 (d,  $J$  = 8.4 Hz, 2H), 4.38 (t,  $J$  = 6.8 Hz, 2H), 1.81 (dt,  $J$  = 14.4, 6.6 Hz, 2H), 1.54 (dt,  $J$  = 14.4, 7.2 Hz, 2H), 1.40 (s, 9H), 1.04 (t,  $J$  = 8.0 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-d)  $\delta$  166.7, 156.4, 129.4, 127.8, 125.2, 64.6, 35.0, 31.1, 30.8, 19.3, 13.7.



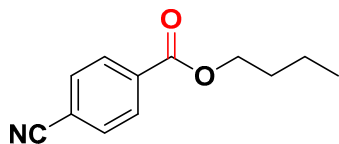
**Butyl [1,1'-biphenyl]-4-carboxylate (3d)** [2] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a light yellow oil (110.5 mg, 87 %);  $^1\text{H}$  NMR (400 MHz, Chloroform-d)  $\delta$  8.19 (d,  $J$  = 8.0 Hz, 2H), 7.44 - 7.69 (m, 4H), 7.54 (t,  $J$  = 8.0 Hz, 2H), 7.47 (t,  $J$  = 7.2 Hz, 2H), 4.43 (t,  $J$  = 6.6 Hz, 2H), 1.85 (dt,  $J$  = 14.4, 6.6 Hz, 2H), 1.58 (dt,  $J$  = 14.4, 7.2 Hz, 2H), 1.07 (t,  $J$  = 8.0 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-d)  $\delta$  166.6, 145.6, 140.1, 130.1, 129.3, 128.9, 128.1, 127.3, 127.0, 64.9, 30.8, 19.3, 13.8.



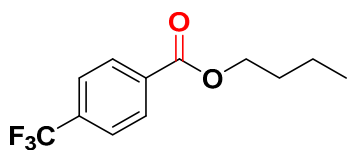
**Butyl 4-hydroxybenzoate (3e)** [3] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a solid (m. p. = 68 - 69 °C ) (79.6 mg, 82 %);  $^1\text{H}$  NMR (400 MHz, Chloroform-d)  $\delta$  7.95 (d,  $J$  = 8.4 Hz, 2H), 6.90 (d,  $J$  = 8.4 Hz, 2H), 4.31 (t,  $J$  = 6.4 Hz, 2H), 1.74 (dt,  $J$  = 14.4, 6.6 Hz, 2H), 1.47 (dt,  $J$  = 14.4, 7.2 Hz, 2H), 0.97 (t,  $J$  = 8.0 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-d)  $\delta$  167.3, 160.5, 131.9, 122.4, 115.3, 64.9, 30.7, 19.2, 13.7.



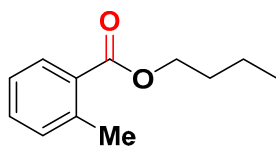
**Butyl 4-iodobenzoate (3f)** [4] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a light yellow oil (89.7 mg, 59 %);  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.86 (d,  $J$  = 8.4 Hz, 2H), 7.80 (d,  $J$  = 8.4 Hz, 2H), 4.37 (t,  $J$  = 6.8 Hz, 2H), 1.80 (dt,  $J$  = 14.6, 6.6 Hz, 2H), 1.54 (dt,  $J$  = 15.0, 7.4 Hz, 2H), 1.04 (t,  $J$  = 8.0 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform- $d$ )  $\delta$  166.1, 137.7, 131.0, 130.0, 100.5, 65.1, 30.7, 19.2, 13.7.



**Butyl 4-cyanobenzoate (3g)** [1] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a colorless solid (m. p. = 53 - 54 °C) (80.2 mg, 79 %);  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.19 (d,  $J$  = 8.4 Hz, 2H), 7.80 (d,  $J$  = 8.4 Hz, 2H), 4.41 (t,  $J$  = 6.6 Hz, 2H), 1.82 (dt,  $J$  = 14.6, 6.7 Hz, 2H), 1.54 (dt,  $J$  = 15.0, 7.4 Hz, 2H), 1.04 (t,  $J$  = 7.4 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform- $d$ )  $\delta$  164.9, 132.1, 130.0, 117.9, 116.3, 65.6, 30.6, 19.2, 13.6.

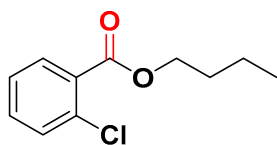


**Butyl 4-(trifluoromethyl)benzoate (3h)** [1] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a yellow oil (100.9 mg, 82 %);  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.16 (d,  $J$  = 8.0 Hz, 2H), 7.70 (d,  $J$  = 8.0 Hz, 2H), 4.37 (t,  $J$  = 6.6 Hz, 2H), 1.77 (dt,  $J$  = 14.4, 6.8 Hz, 1H), 1.49 (dt,  $J$  = 15.0, 7.4 Hz, 2H), 0.99 (t,  $J$  = 8.0 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform- $d$ )  $\delta$  165.4, 134.3 (q,  $J$  = 32.6 Hz), 133.8, 129.9, 125.3 (q,  $J$  = 3.7 Hz), 123.7 (q,  $J$  = 271.0 Hz), 65.4, 30.7, 19.2, 13.7.

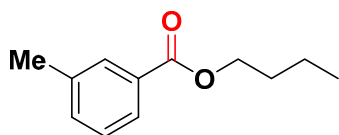


**Butyl 2-methylbenzoate (3i)** [1] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a colorless oil (85.5 mg, 89 %);  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.98 (d,  $J$  = 8.0 Hz, 1H), 7.45 (t,  $J$  = 8.0 Hz, 1H), 7.32 - 7.29 (m, 2H), 4.37 (t,  $J$  = 6.8 Hz, 2H), 2.67 (s,

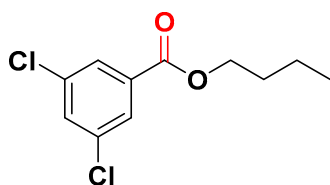
3H), 1.82 (dt,  $J = 14.6, 6.8$  Hz, 2H), 1.56 (dt,  $J = 15.0, 7.2$  Hz, 2H), 1.05 (t,  $J = 8.0$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-d)  $\delta$  167.8, 140.0, 131.7, 131.6, 130.5, 130.1, 125.6, 64.6, 30.8, 21.7, 19.3, 13.7.



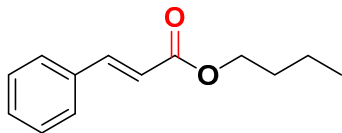
**Butyl 2-chlorobenzoate (3j)** [1] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a yellow oil (89.1 mg, 84 %);  $^1\text{H}$  NMR (400 MHz, Chloroform-d)  $\delta$  8.07 (d,  $J = 8.0$  Hz, 1H), 8.00 - 7.98 (m, 1H), 7.60 - 7.57 (m, 1H), 7.44 (t,  $J = 8.0$  Hz, 1H), 4.39 (t,  $J = 6.8$  Hz, 2H), 1.82 (dt,  $J = 14.4, 6.8$  Hz, 2H), 1.56 (dt,  $J = 15.0, 7.2$  Hz, 2H), 1.04 (t,  $J = 8.0$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-d)  $\delta$  134.5, 132.8, 132.3, 129.6, 127.7, 102.0, 65.2, 30.7, 19.2, 13.7.



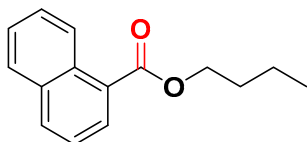
**Butyl 3-methylbenzoate (3k)** [1] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a colorless oil (84.5 mg, 88 %);  $^1\text{H}$  NMR (400 MHz, Chloroform-d)  $\delta$  7.91 (d,  $J = 8.8$  Hz, 2H), 7.43 - 7.37 (m, 2H), 4.38 (t,  $J = 6.6$  Hz, 3H), 2.47 (s, 3H), 1.82 (dt,  $J = 14.6, 6.7$  Hz, 2H), 1.56 (dt,  $J = 15.0, 7.4$  Hz, 2H), 1.05 (t,  $J = 8.0$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-d)  $\delta$  166.9, 138.1, 133.5, 130.5, 130.0, 128.2, 126.7, 64.7, 30.8, 21.2, 19.3, 13.7.



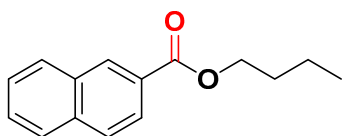
**Butyl 3,5-dichlorobenzoate (3l)** [5] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a yellow oil (102.1 mg, 83 %);  $^1\text{H}$  NMR (400 MHz, Chloroform-d)  $\delta$  7.95 (s, 2H), 7.59 (s, 1H), 4.39 (t,  $J = 6.6$  Hz, 2H), 1.81 (dt,  $J = 14.4, 6.8$  Hz, 2H), 1.54 (dt,  $J = 15.0, 7.4$  Hz, 2H), 1.04 (t,  $J = 8.0$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-d)  $\delta$  164.3, 135.2, 133.4, 132.6, 128.0, 65.7, 30.6, 19.2, 13.7.



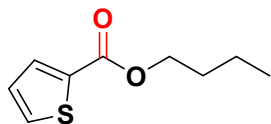
**Butyl cinnamate (3m)** [3] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a yellow solid (m. p. = 139 - 140 °C) (74.5 mg, 73 %);  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.75 (d,  $J$  = 16.0 Hz, 1H), 7.60 - 7.58 (m, 4H), 7.45 - 7.44 (m, 3H), 6.51 (d,  $J$  = 16.0 Hz, 1H), 4.28 (t,  $J$  = 6.8 Hz, 2H), 1.76 (dt,  $J$  = 14.4, 6.8 Hz, 2H), 1.52 (dt,  $J$  = 15.0, 7.4 Hz, 2H), 1.03 (t,  $J$  = 8.0 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform- $d$ )  $\delta$  167.0, 144.5, 134.5, 130.1, 128.8, 128.0, 118.3, 64.4, 30.8, 19.2, 13.7.



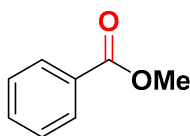
**Butyl 1-naphthoate (3n)** [2] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a yellow oil (95.8 mg, 84 %);  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  9.00 (d,  $J$  = 8.0 Hz, 1H), 8.27 - 8.25 (m, 1H), 8.08 (d,  $J$  = 8.0 Hz, 1H), 7.95 (d,  $J$  = 8.0 Hz, 1H), 7.71 - 7.67 (m, 1H), 7.62 - 7.55 (m, 2H), 4.51 (d,  $J$  = 6.6 Hz, 2H), 1.93 - 1.86 (m, 2H), 1.65 - 1.56 (m, 2H), 1.08 (t,  $J$  = 7.4 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform- $d$ )  $\delta$  167.7, 133.9, 133.1, 131.4, 130.0, 128.5, 127.6, 126.1, 125.8, 124.5, 64.9, 30.8, 19.4, 13.7.



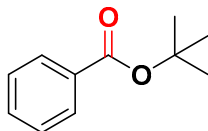
**Butyl 2-naphthoate (3o)** [5] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a yellow solid (m. p. = 41 - 42 °C) (96.9 mg, 85 %);  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.68 (s, 1H), 8.15 - 8.13 (m, 1H), 8.03 (d,  $J$  = 8.0 Hz, 1H), 7.95 (d,  $J$  = 8.0 Hz, 2H), 7.67 - 7.59 (m, 2H), 4.46 (t,  $J$  = 6.6 Hz, 2H), 1.88 (dt,  $J$  = 14.6, 6.7 Hz, 2H), 1.59 (dt,  $J$  = 15.0, 7.4 Hz, 2H), 1.08 (d,  $J$  = 8.0 Hz, 2H);  $^{13}\text{C}$  NMR (100MHz, Chloroform- $d$ )  $\delta$  166.8, 135.5, 132.5, 130.9, 129.3, 128.1, 127.7, 126.5, 125.2, 65.0, 30.8, 19.3, 13.8.



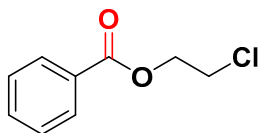
**Butyl thiophene-2-carboxylate (3p)** [5] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a yellow oil (80.1 mg, 87 %);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.86 - 7.85 (m, 1H), 7.61 - 7.59 (m, 1H), 7.17 - 7.14 (m, 1H), 4.36 (t,  $J$  = 6.6 Hz, 2H), 1.83 - 1.76 (m, 2H), 1.57 - 1.49 (m, 2H), 1.03 (t,  $J$  = 7.4 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  162.3, 134.2, 133.2, 132.1, 127.6, 65.0, 30.7, 19.2, 13.7.



**Methyl benzoate (4a)** [1] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a white solid (M. p.=116-117 °C) (57.8 mg, 85%);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.11 (d,  $J$  = 8.0 Hz, 2H), 7.62 (t,  $J$  = 8.0 Hz, 1H), 7.50 (t,  $J$  = 8.0 Hz, 2H), 3.98 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  167.1, 132.8, 130.2, 129.5, 128.3, 52.0.



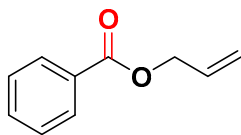
**tert-Butyl benzoate (4b)** [6] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a white solid (M. p.=97-98 °C ) (68.6 mg, 77%);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.06 (d,  $J$  = 8.0 Hz, 2H), 7.59 (t,  $J$  = 8.0 Hz, 1H), 7.48 (t,  $J$  = 8.0 Hz, 2H), 1.66 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  165.8, 132.4, 132.1, 129.4, 128.1, 28.2.



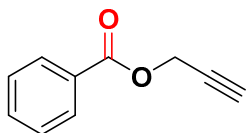
**2-Chloroethyl benzoate (4c)** [5] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a colorless oil (73.6 mg, 80%);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$



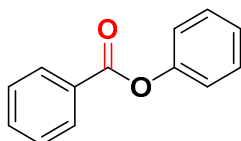
8.07 (d,  $J = 8.0$  Hz, 2H), 7.58 (t,  $J = 8.0$  Hz, 1H), 7.45 (t,  $J = 8.0$  Hz, 2H), 4.57 (t,  $J = 6.0$  Hz, 2H), 3.82 (t,  $J = 6.0$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform- $d$ )  $\delta$  166.1, 133.2, 129.7, 129.6, 128.4, 64.4, 41.6.



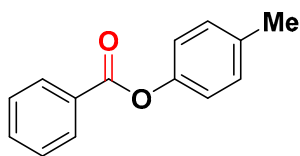
**Allyl benzoate (4d)** [7] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a white solid (M. p.=138-139 °C) (65.6 mg, 81 %);  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.15 - 8.12 (m, 2H), 7.65 - 7.61 (m, 1H), 7.51 (t,  $J = 8.0$  Hz, 2H), 6.16 - 6.06 (m, 1H), 5.51 - 5.46 (m, 1H), 5.37 - 5.34 (m, 1H), 4.91 - 4.89 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform- $d$ )  $\delta$  166.2, 132.9, 132.3, 130.2, 129.6, 128.3, 118.2, 65.5.



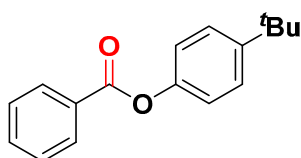
**Prop-2-yn-1-yl benzoate (4e)** [7] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a white solid (M. p.=120-121 °C) (57.6 mg, 72 %);  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.14 (d,  $J = 8.0$  Hz, 2H), 7.66 - 7.62 (m, 1H), 7.52 (t,  $J = 8.0$  Hz, 2H), 4.99 (d,  $J = 2.5$  Hz, 1H), 2.59 (t,  $J = 2.4$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform- $d$ )  $\delta$  165.8, 133.3, 129.8, 129.4, 128.4, 77.7, 75.0, 52.4.



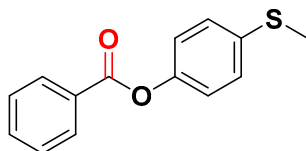
**Phenyl benzoate (4f)** [6] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a white solid (M. p.=124-125 °C) (89.1mg, 90 %);  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.31 - 8.29 (m, 2H), 7.74 - 7.70 (m, 1H), 7.61 - 7.58 (m, 2H), 7.54 - 7.50 (m, 2H), 7.38 - 7.30 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform- $d$ )  $\delta$  165.1, 151.0, 133.5, 130.1, 129.5, 128.5, 125.8, 121.7, 101.9.



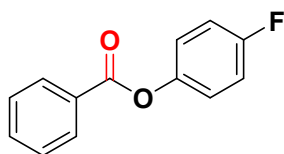
***p*-Tolyl benzoate (4g)** [8] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a white solid (M. p.=127-128 °C) (93.3 mg, 88 %); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.30 - 8.27 (m, 2H), 7.71 (t, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 2.46 (s, 3H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*)  $\delta$  165.3, 148.8, 135.5, 133.4, 130.1, 130.0, 128.5, 121.3, 102.0, 20.9.



**4-(*tert*-Butyl)phenyl benzoate (4h)** [8] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a white solid (M. p.=107 - 108 °C) (110.5 mg, 87 %); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.30 - 8.28 (m, 2H), 7.71 (t, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.53 - 7.51 (m, 1H), 7.23 - 7.21 (m, 2H), 1.42 (s, 9H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*)  $\delta$  165.3, 148.7, 133.4, 130.1, 129.8, 128.5, 126.3, 121.0, 102.0, 34.5, 31.4.

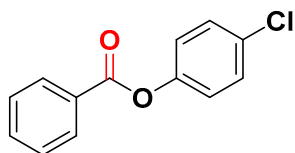


**4-(Methylthio)phenyl benzoate (4i)** [9] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a white solid (M.p.=94-96 °C) (108.6 mg, 89 %); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.27 (d, *J* = 8.0 Hz, 2H), 7.71 (t, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 2.57 (s, 3H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*)  $\delta$  165.1, 148.7, 135.7, 133.6, 130.1, 129.5, 128.5, 128.1, 122.1, 16.5.

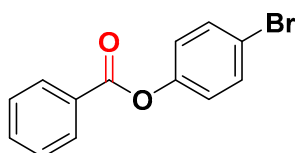


**4-Fluorophenyl benzoate (4j)** [10] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a yellow oil (90.7 mg, 84 %); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$

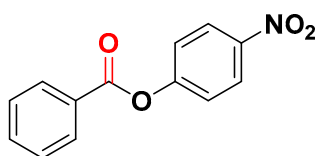
8.27 (d,  $J = 8.0$  Hz, 2H), 7.72 (t,  $J = 8.0$  Hz, 1H), 7.59 (t,  $J = 8.0$  Hz, 2H), 7.27 - 7.24 (m, 2H), 7.21 - 7.16 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  165.2, 160.3 (d,  $J = 244.2$  Hz), 146.8, 133.7, 130.2, 128.6, 123.1 (d,  $J = 8.1$  Hz), 116.1 (d,  $J = 23.4$  Hz), 102.0.



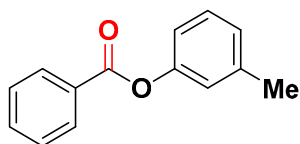
**4-Chlorophenyl benzoate (4k)** [8] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a white solid (M. p.=177 - 178 °C) (95.1 mg, 82 %);  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.27 (d,  $J = 8.0$  Hz, 2H), 7.72 (t,  $J = 8.0$  Hz, 1H), 7.59 (t,  $J = 8.0$  Hz, 2H), 7.48 - 7.45 (m, 2H), 7.25 - 7.23 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform- $d$ )  $\delta$  164.9, 149.5, 133.8, 131.3, 130.2, 129.6, 128.6, 123.1, 102.0.



**4-Bromophenyl benzoate (4l)** [11] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a white solid (M. p.=115 - 116 °C) (109.0 mg, 79 %);  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.26 (d,  $J = 8.0$  Hz, 2H), 7.72 (t,  $J = 8.0$  Hz, 1H), 7.63 - 7.57 (m, 4H), 7.20 - 7.18 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  164.8, 150.0, 133.8, 132.5, 130.2, 129.2, 128.6, 123.5, 118.9.



**4-Nitrophenyl benzoate (4m)** [11] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a white solid (M. p.=143 - 144 °C) (88.7 mg, 73 %);  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.41 - 8.38 (m, 2H), 8.28 - 8.26 (m, 2H), 7.75 (t,  $J = 8.0$  Hz, 1H), 7.61 (t,  $J = 8.0$  Hz, 2H), 7.51 - 7.48 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform- $d$ )  $\delta$  164.2, 155.7, 145.4, 134.2, 130.3, 128.8, 128.6, 125.2, 122.6.

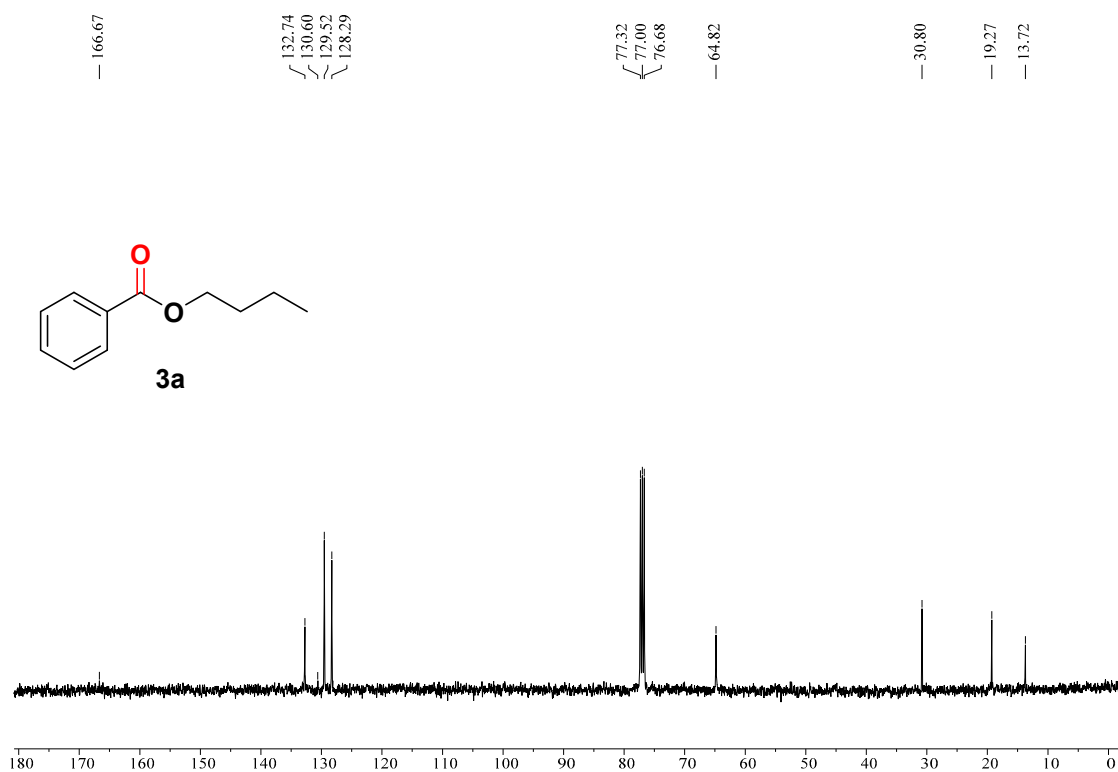
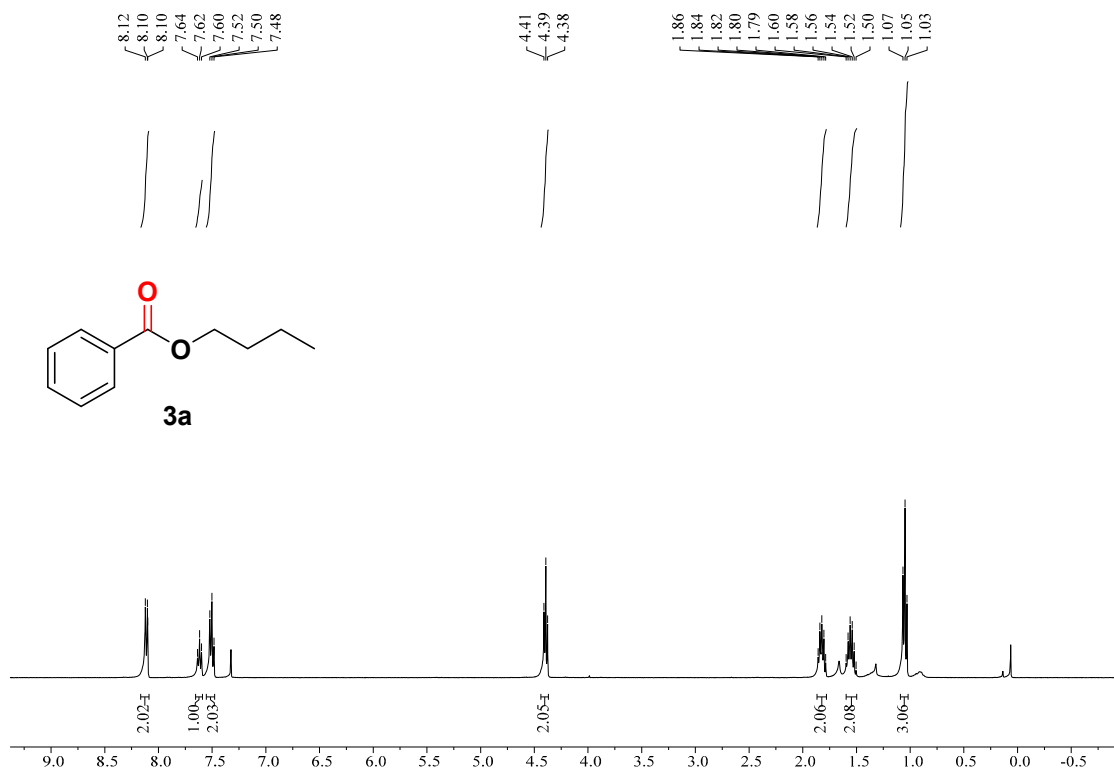


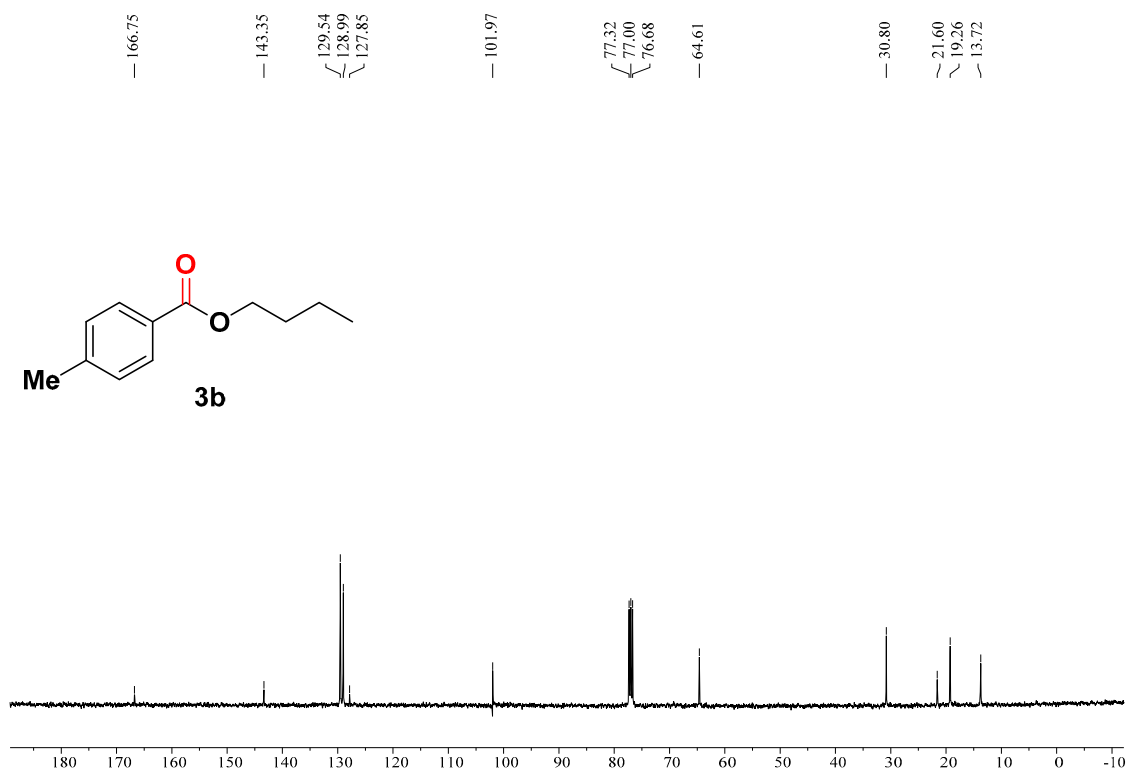
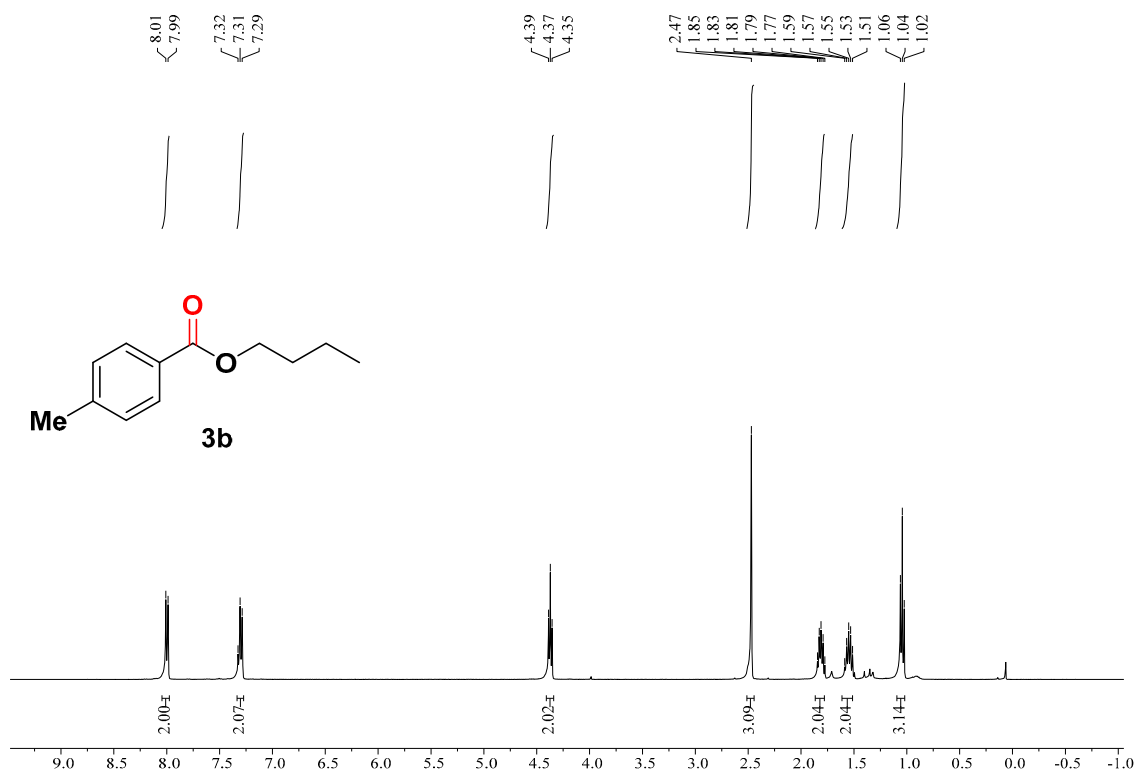
***m*-Tolyl benzoate (4n)** [8] was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate) as a white solid (M. p.=150 - 151 °C) (90.1 mg, 85 %); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.29 (d, *J* = 8.0 Hz, 2H), 7.71 (t, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.18 - 7.09 (m, 3H), 2.47 (s, 3H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*)  $\delta$  165.2, 151.0, 139.6, 133.5, 130.1, 129.7, 129.2, 128.5, 126.6, 122.3, 118.6, 21.3.

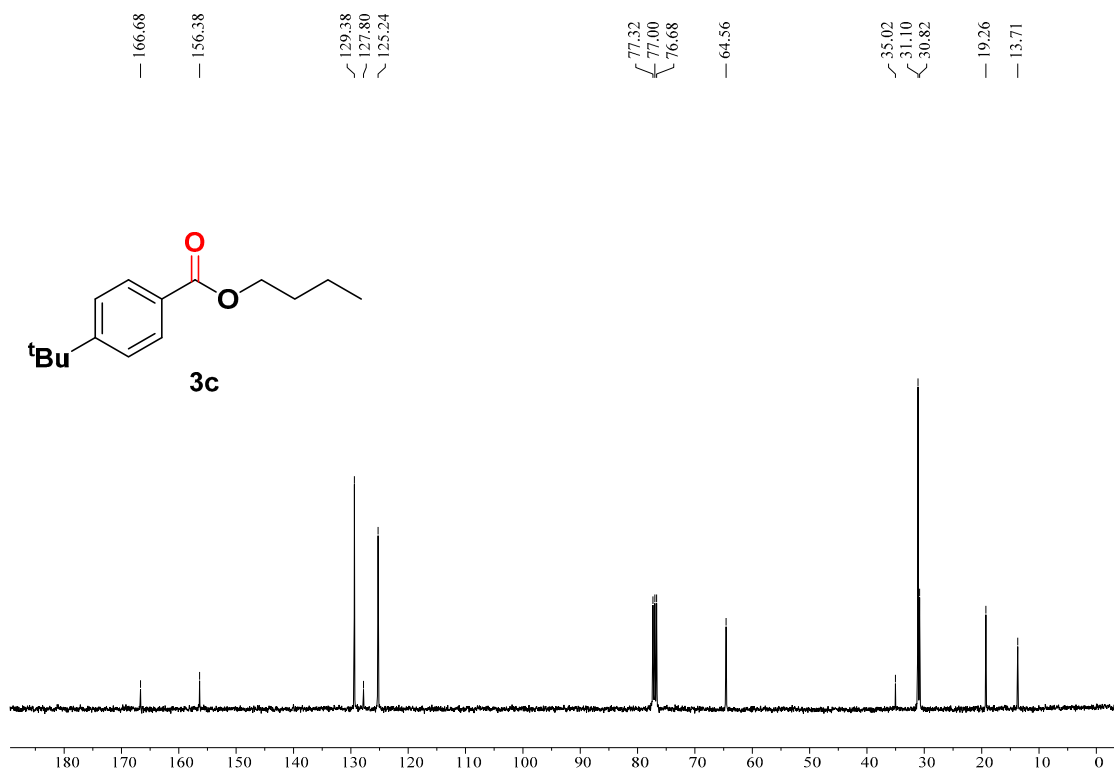
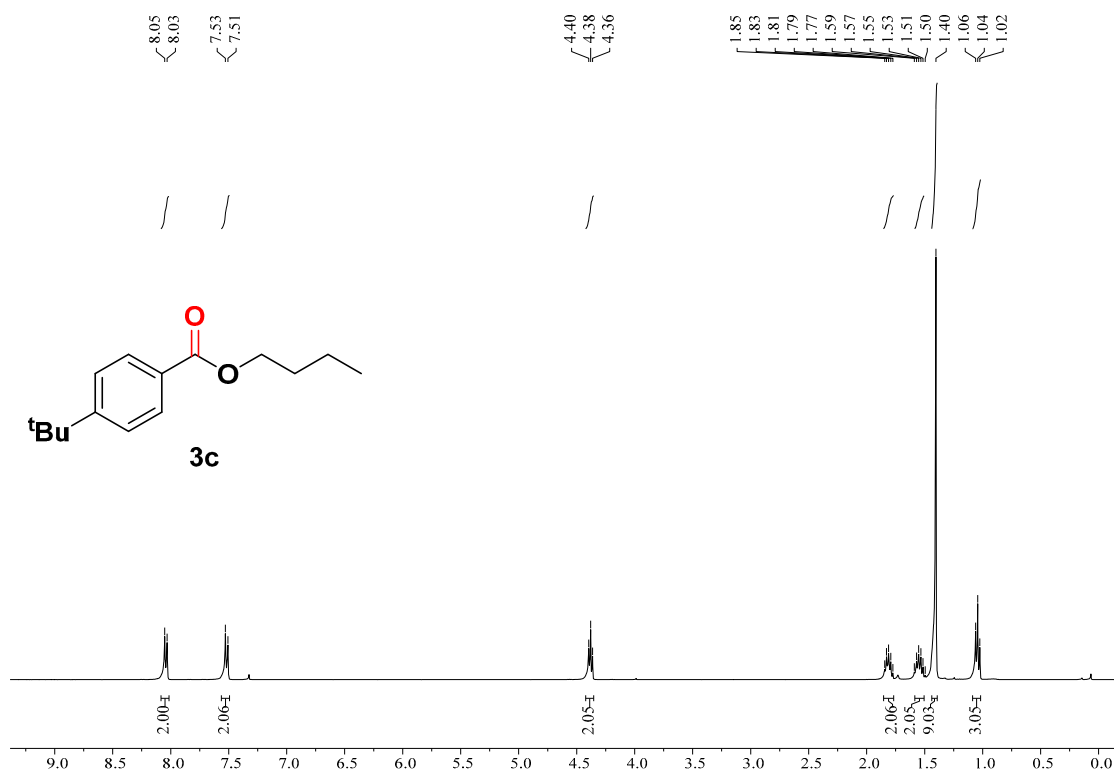
## References

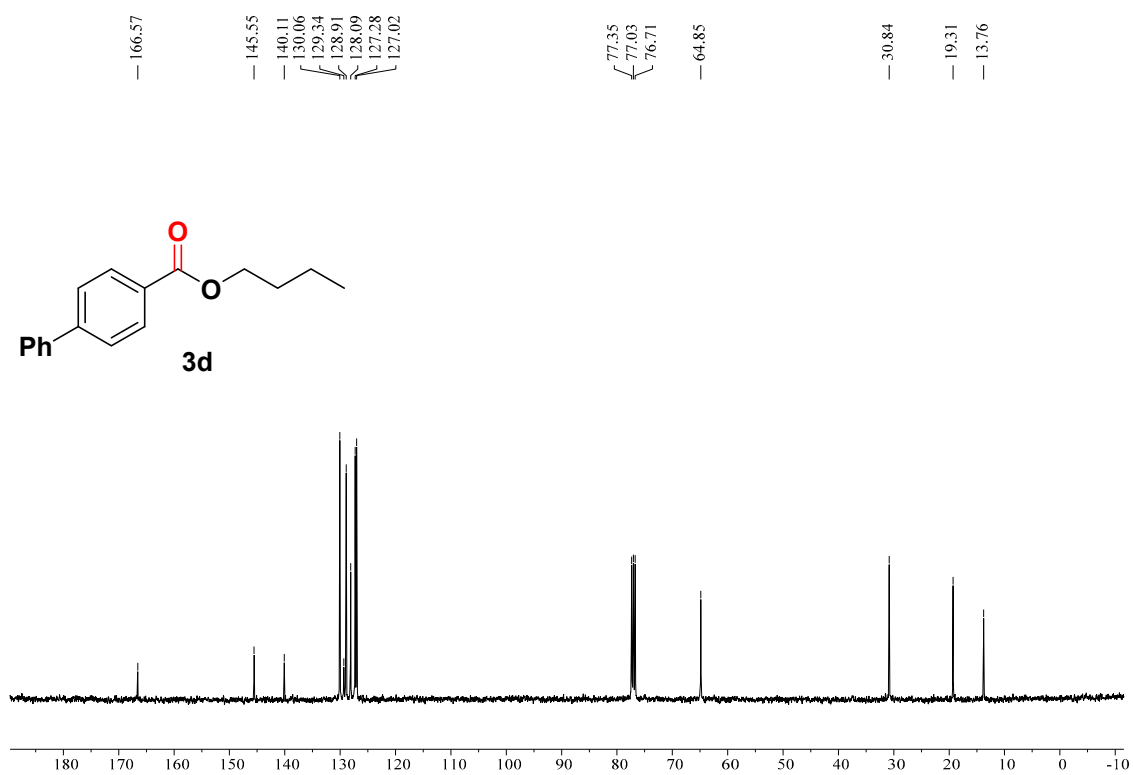
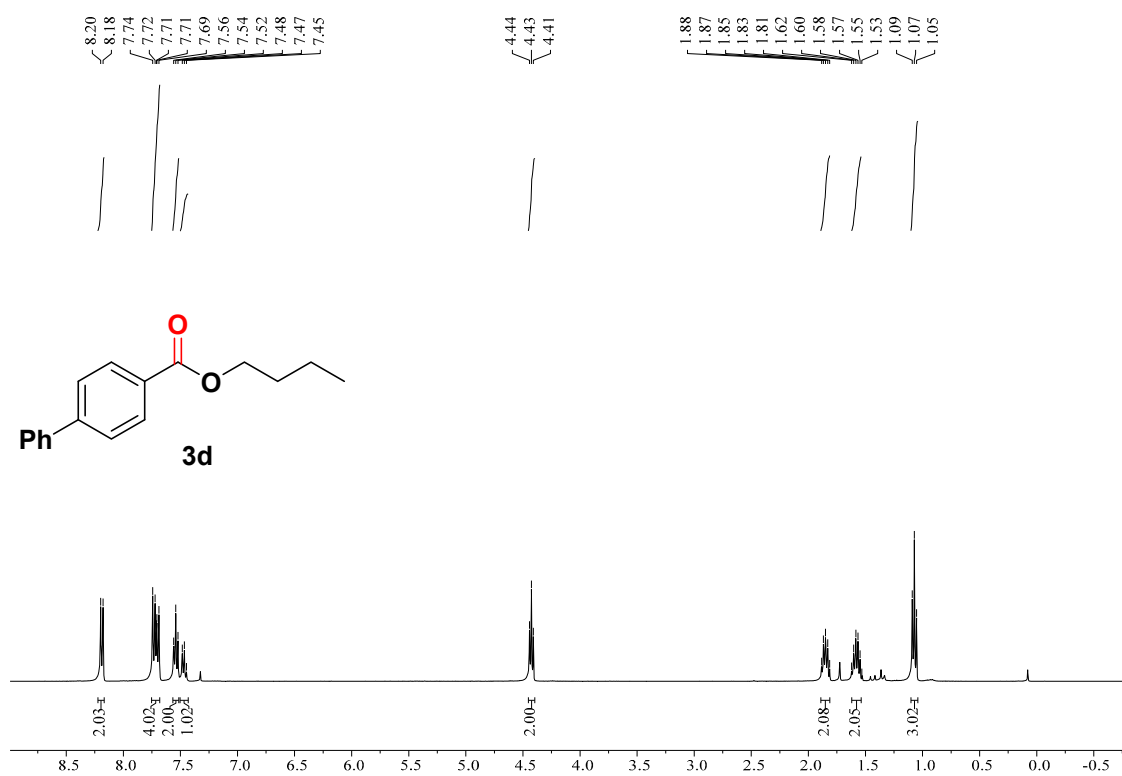
- Kong, W.; Li, B.; Xu, X.; Song, Q. Fe-Catalyzed Aerobic Oxidative C–CN Bond Cleavage of Arylacetonitriles Leading to Various Esters. *J. Org. Chem.* **2016**, *81*, 8436–8441.
- Nakatani, Y.; Koizumi, Y.; Yamasaki, Y.; Saito, S. Copper-Catalyzed Synthesis of Esters from Ketones. Alkyl Group as a Leaving Group. *Org. Lett.* **2008**, *10*, 2067–2071.
- Iwasaki, T.; Maegawa, Y.; Hayashi, Y.; Ohshima, T.; Mashima, K. Transesterification of Various Methyl Esters Under Mild Conditions Catalyzed by Tetranuclear Zinc Cluster. *J. Org. Chem.* **2008**, *73*, 5147–5150.
- Corma, A.; Villoria-del-Álamo, B.; Rojas-Buzo, S.; García-García, P. Zr-MOF-808 as Catalyst for Amide Esterification. *Chem. Eur. J.* **2021**, *27*, 4588–4598.
- Yuan, Y.; Wu, X.-F. Synthesis of Esters from Stable and Convenient Sulfoxonium Precursors under Catalyst- and Additive-Free Conditions. *Synlett.* **2019**, *30*, 1820–1824.
- Ibrahim, M. B.; Suleiman, R. K.; Fettouhi, M.; El Ali, B. A palladium-bisoxazoline supported catalyst for selective synthesis of aryl esters and aryl amides via carbonylative coupling reactions. *RSC Adv.* **2016**, *6*, 78826–78837.
- Chen, Z.; Wen, Y.; Fu, Y.; Chen, H.; Ye, M.; Luo, G. Graphene Oxide: An Efficient Acid Catalyst for the Construction of Esters from Acids and Alcohols. *Synlett.* **2017**, *28*, 981–985.
- Liu, J.; Chen, J.; Xia, C. A simple and efficient recyclable phosphine-free catalytic system for alkoxy carbonylation and carbonylative Sonogashira coupling reactions of aryl iodides. *J. Catal.* **2008**, *253*, 50–56.
- Wu, X.-F.; Neumann, H.; Beller, M. A General and Efficient Palladium-Catalyzed Alkoxy carbonylation of Phenols To Form Esters through In Situ Formed Aryl Nonaflates. *Chem. Eur. J.* **2012**, *18*, 3831–3834.
- Chai, L.; Zhao, Y.-H.; Young, D. J.; Lu, X.; Li, H.-X. Ni(II)-Mediated Photochemical Oxidative Esterification of Aldehydes with Phenols. *Org. Lett.* **2022**, *24*, 6908–6913.
- Liao, W.-J.; Lin, S.-Y.; Kuo, Y.-S.; Liang, C.-F. Site-Selective Acylation of Phenols Mediated by a Thioacid Surrogate through Sodium Thiosulfate Catalysis. *Org. Lett.* **2022**, *24*, 4207–4211.

## NMR spectra for all the compounds

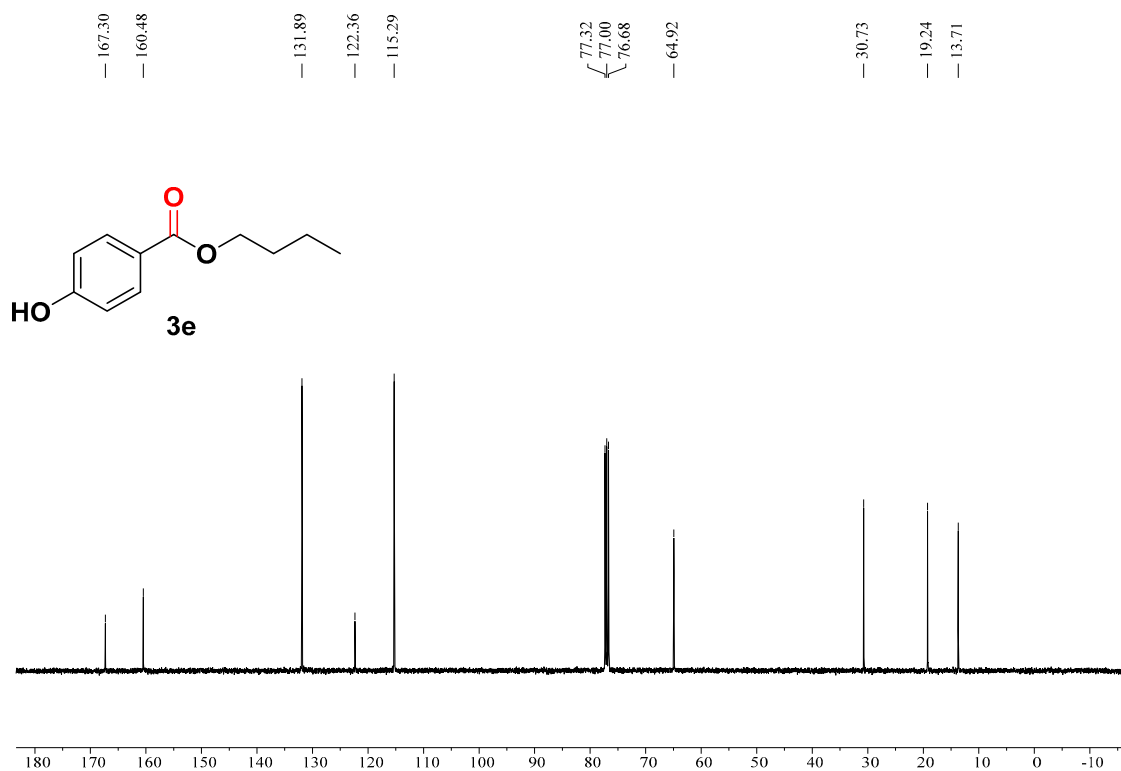
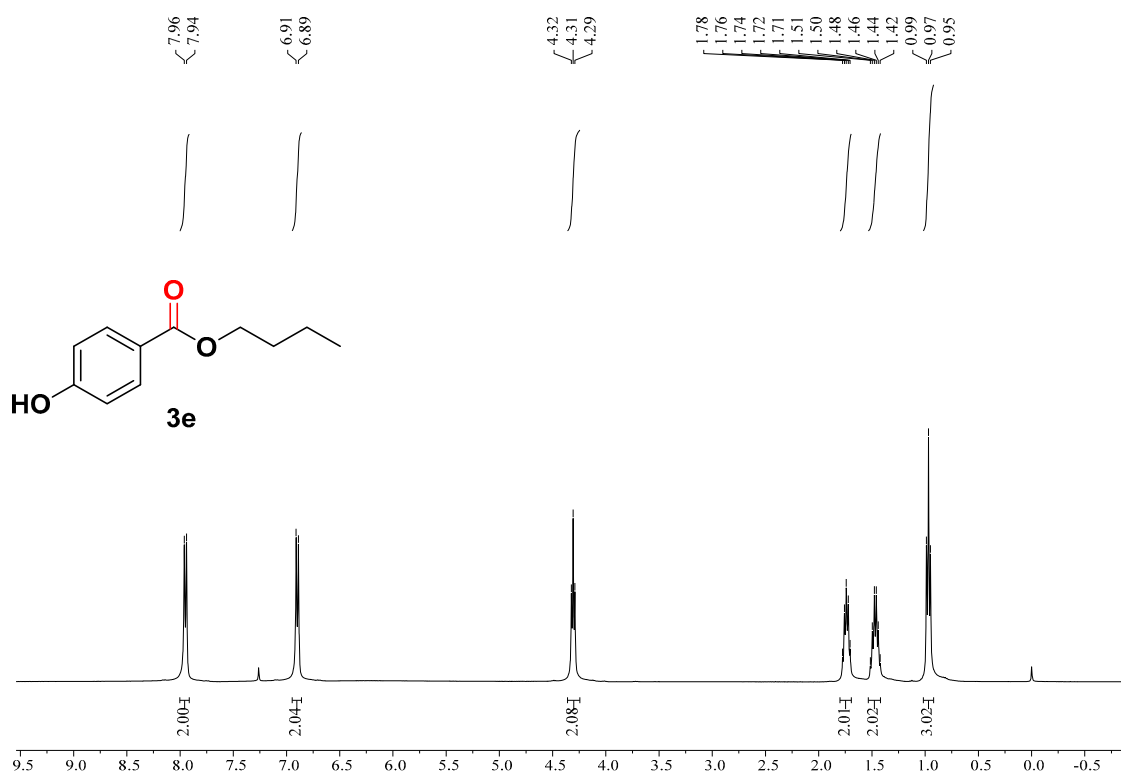


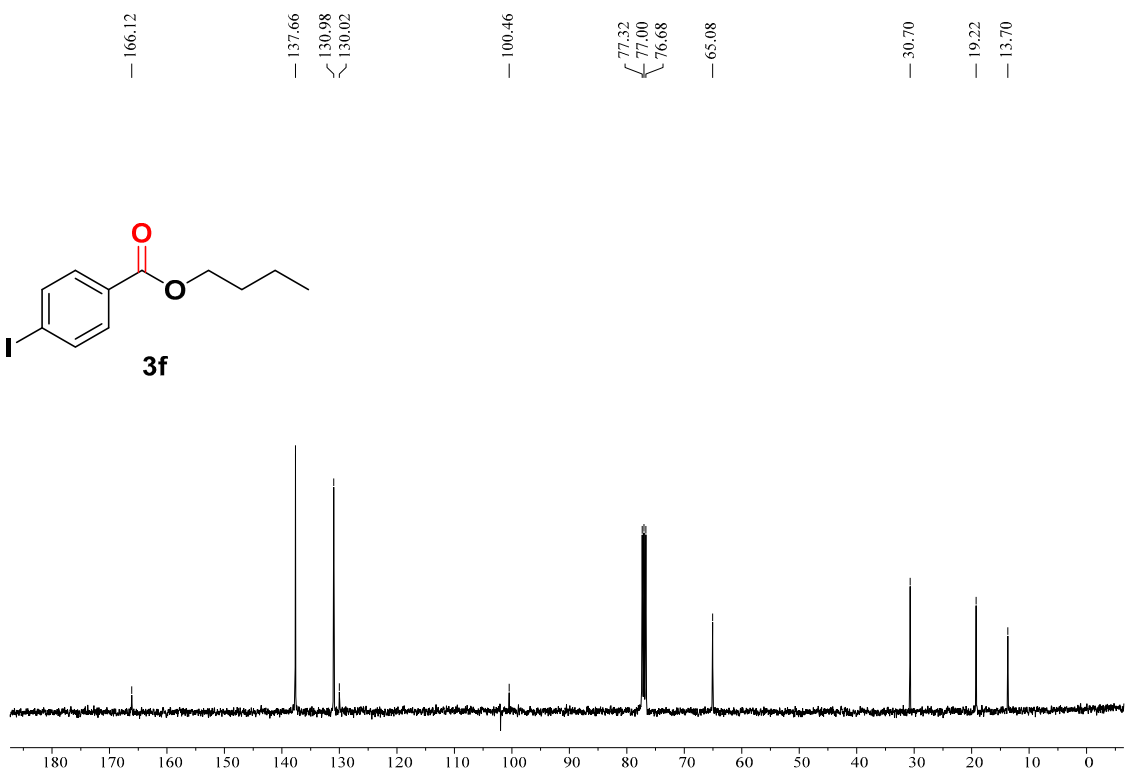
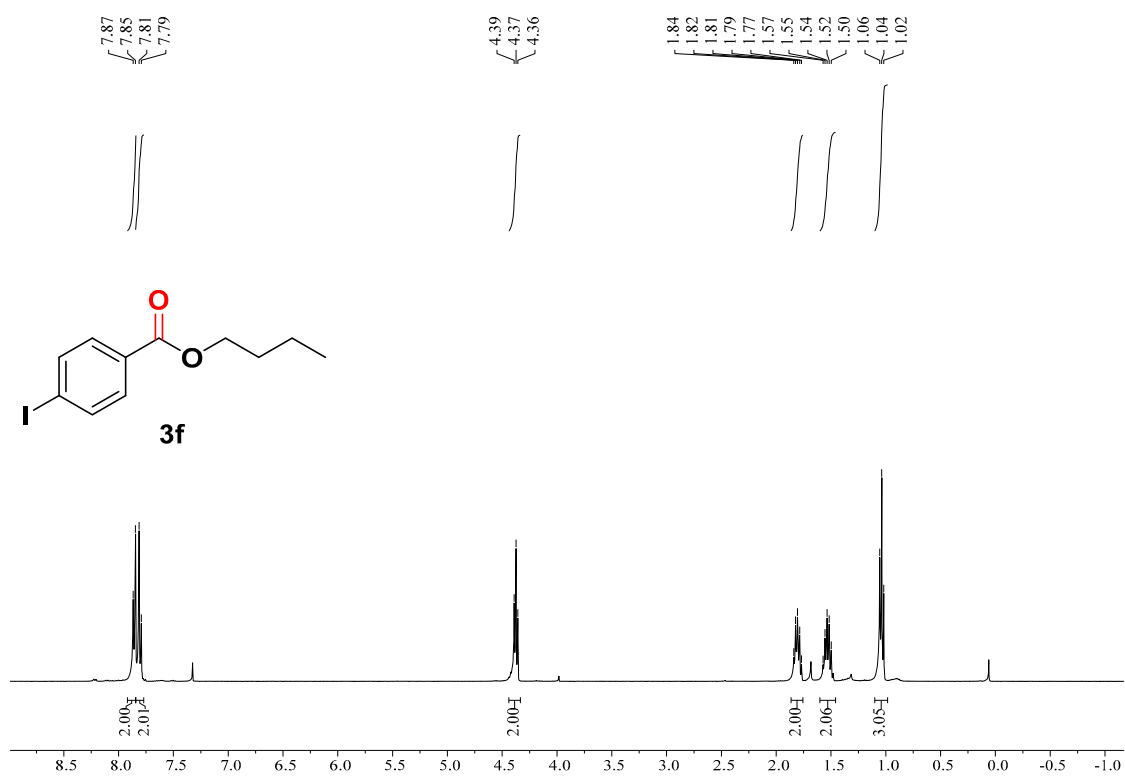


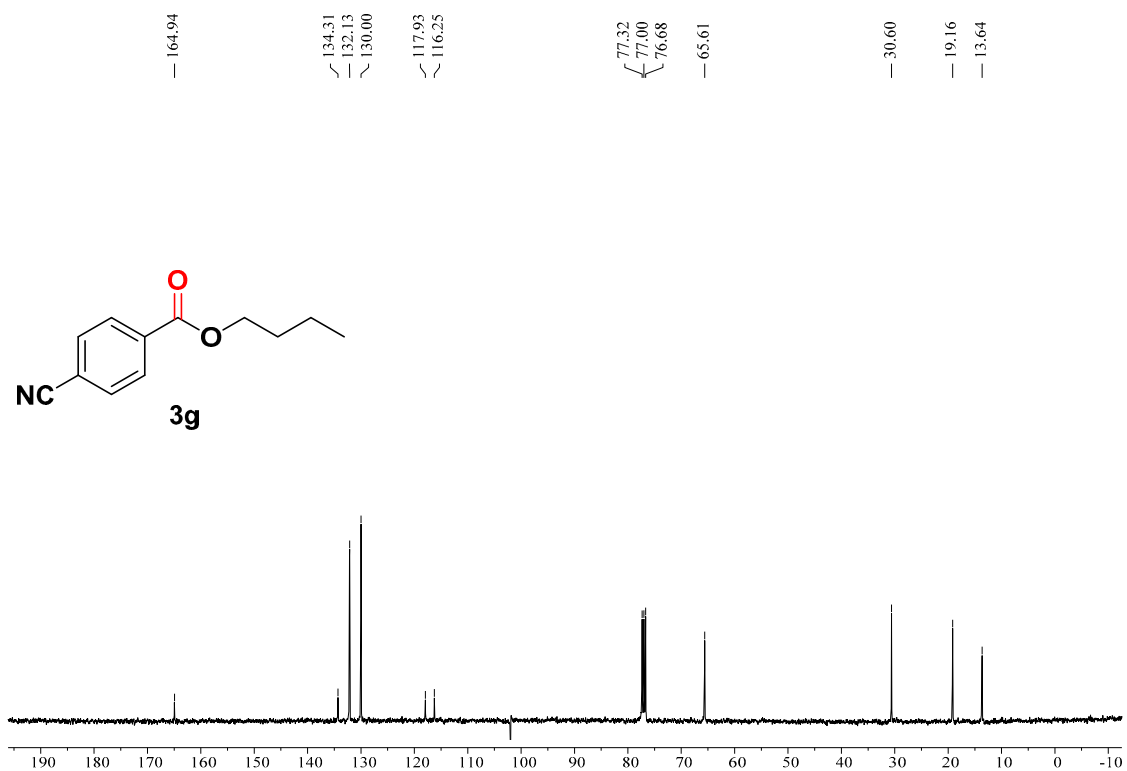
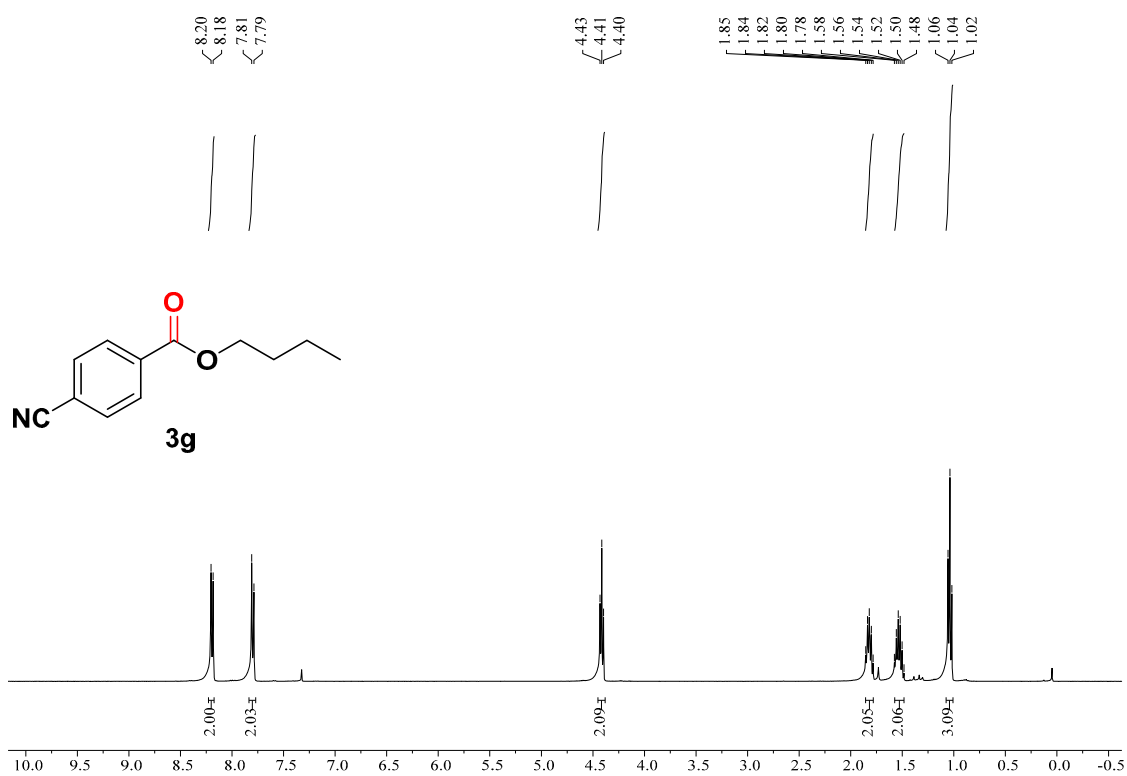


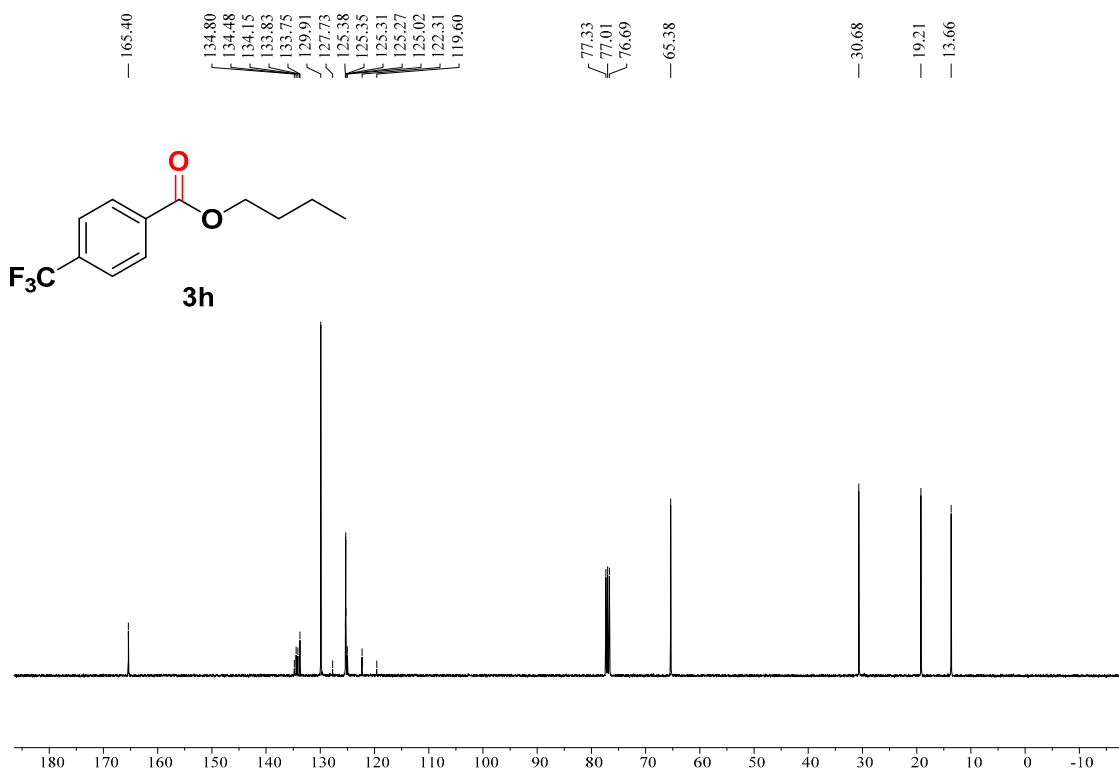
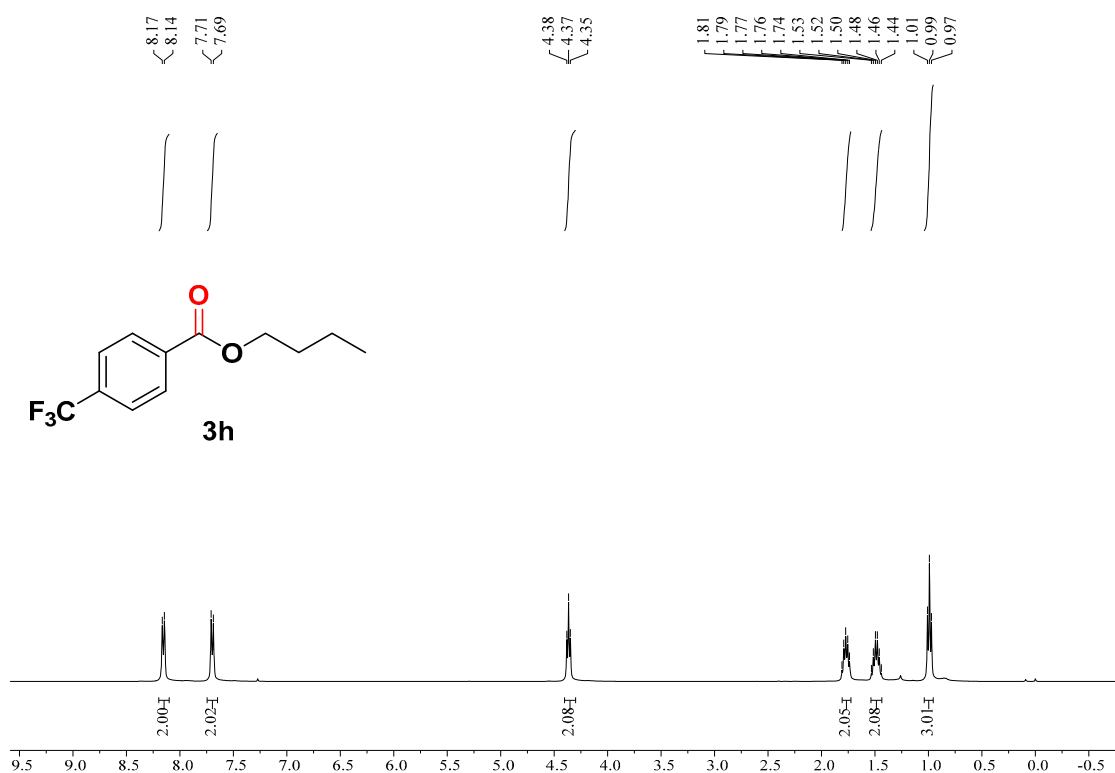


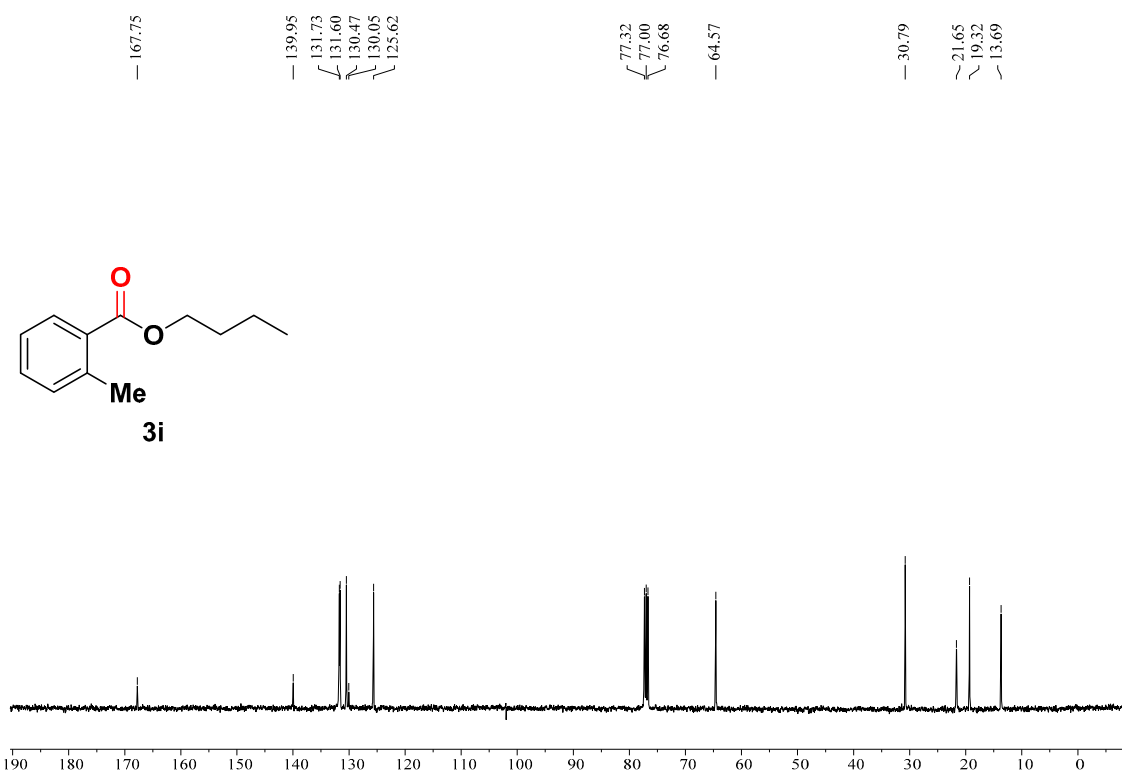
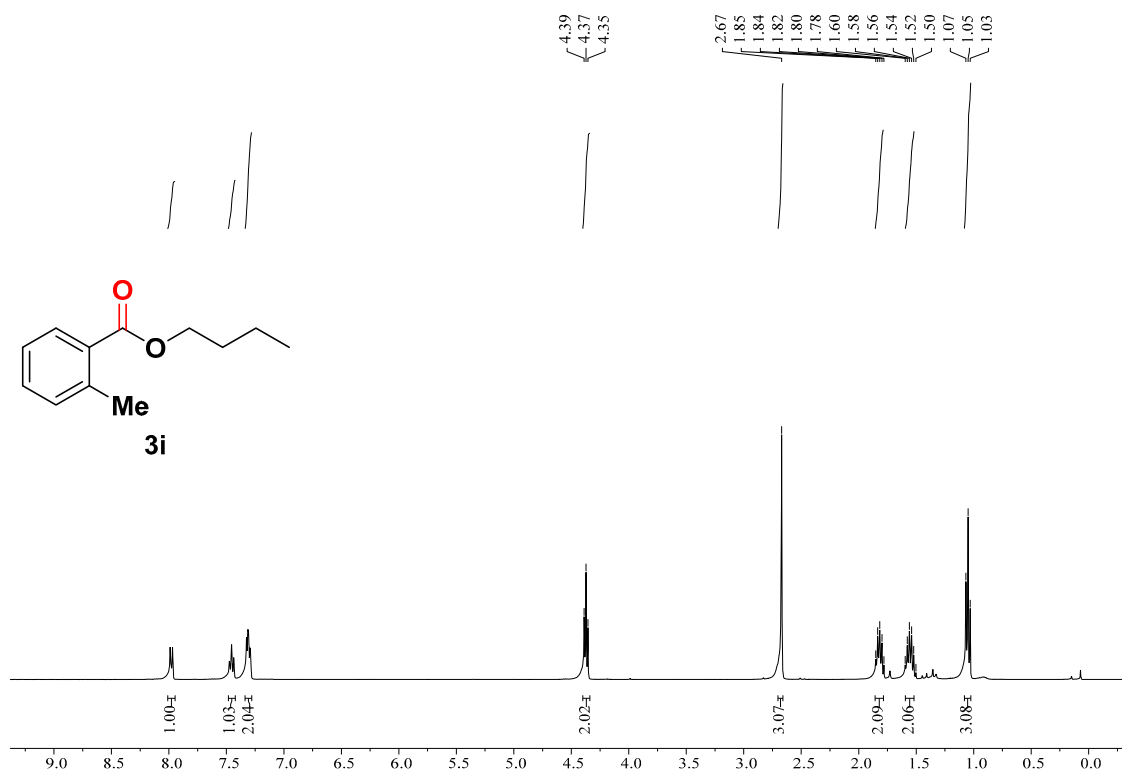


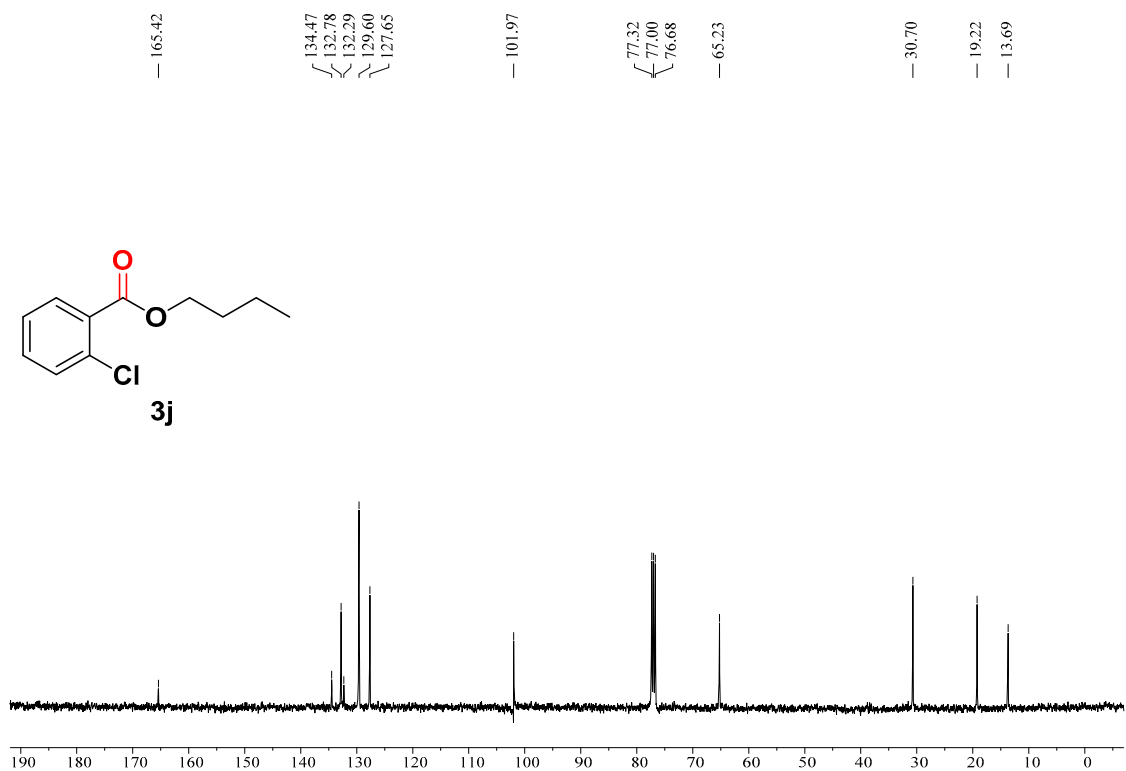
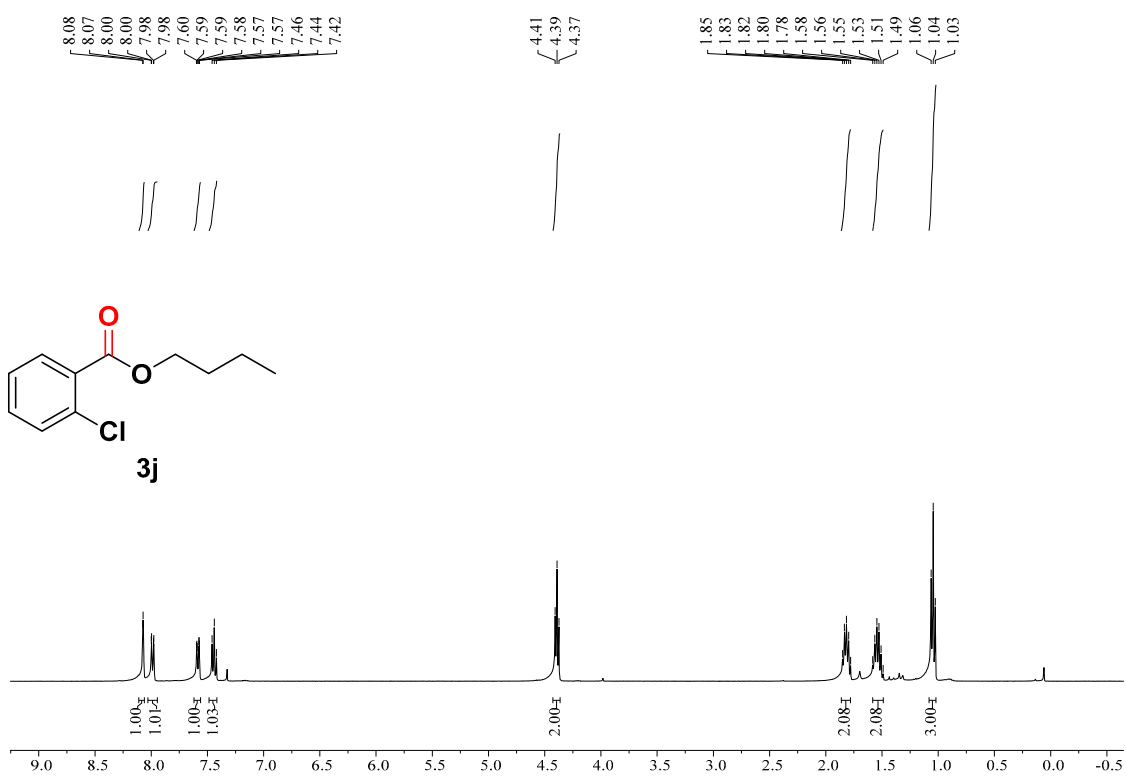


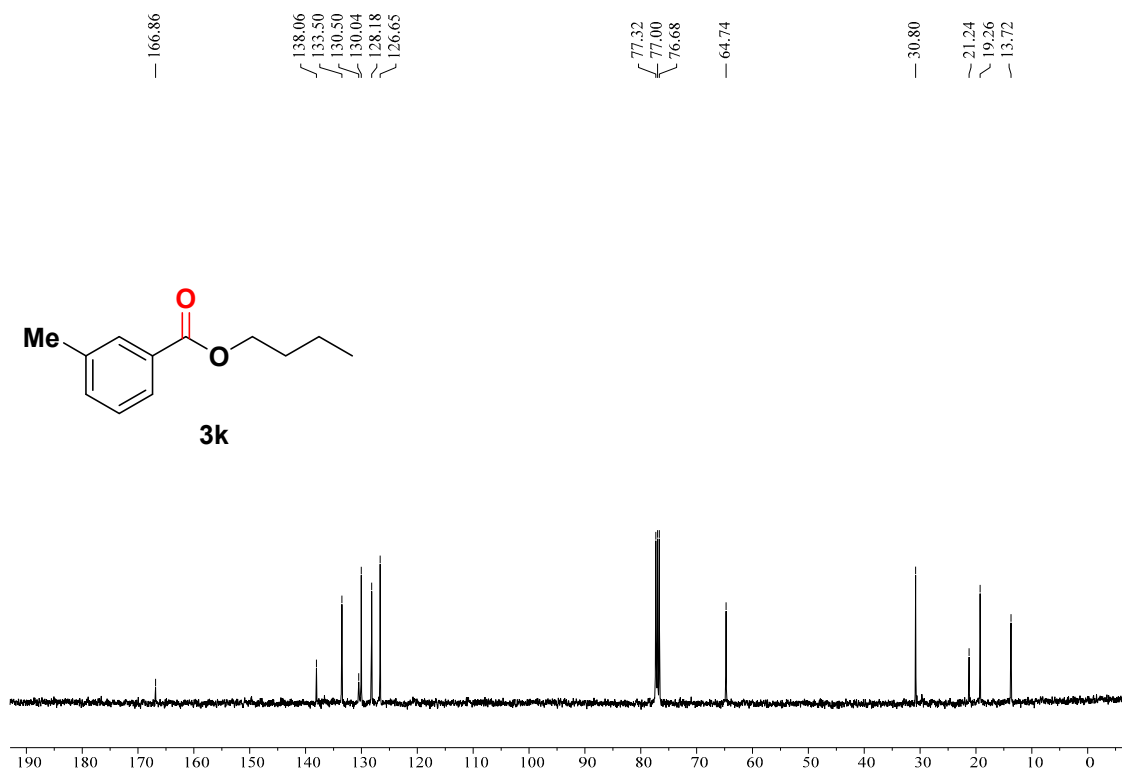
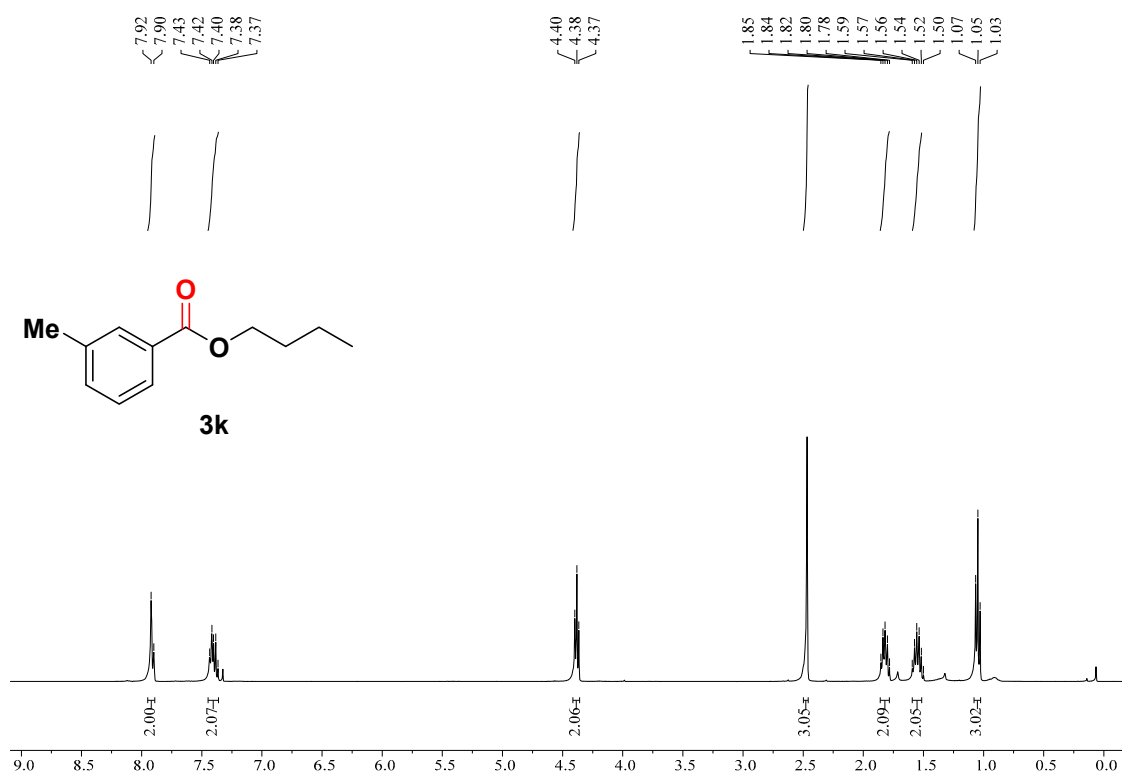


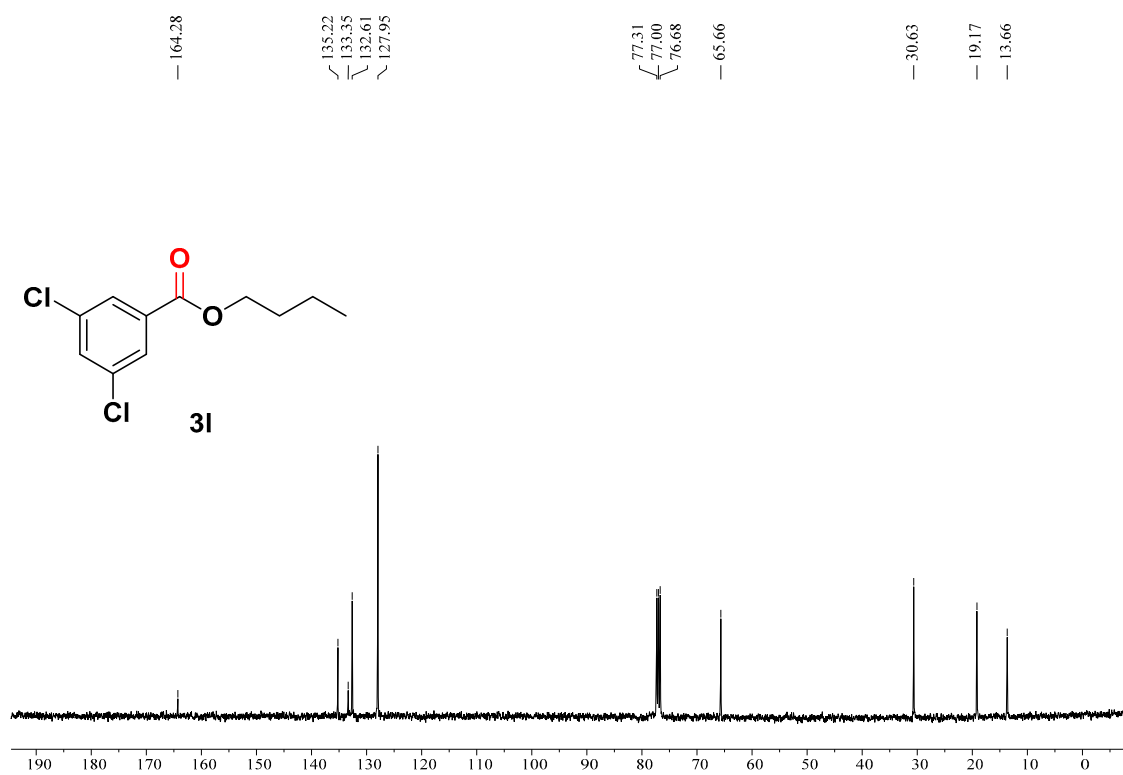
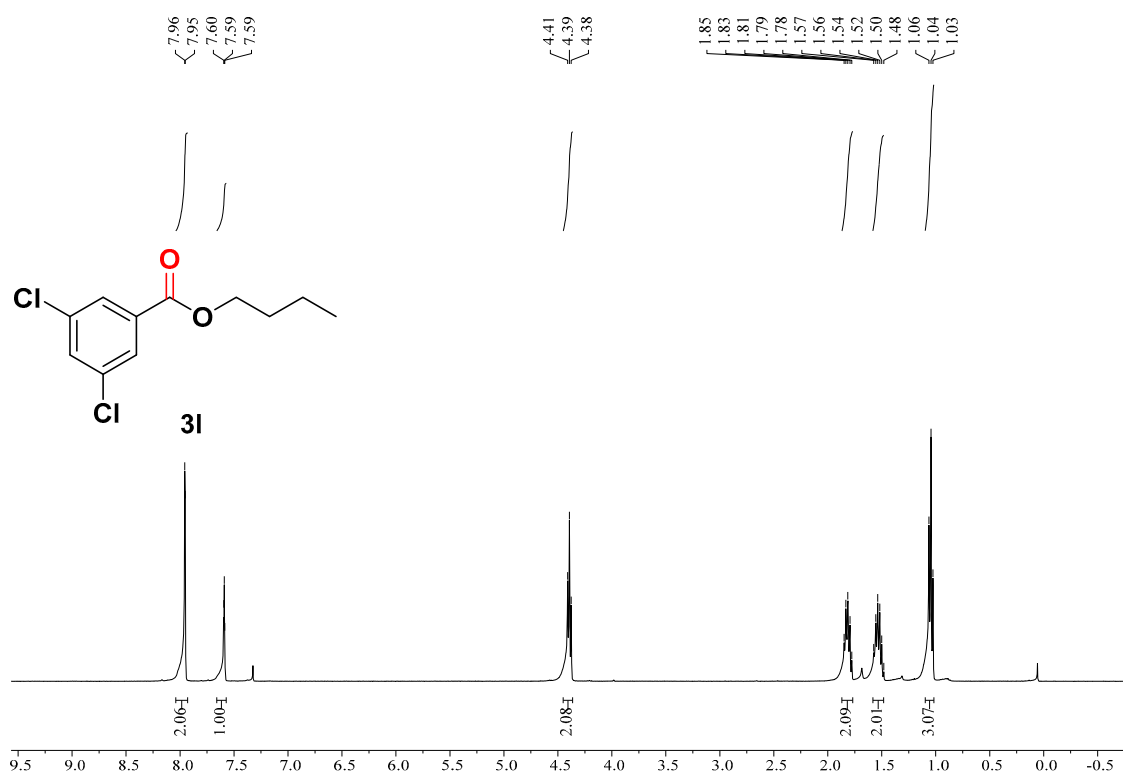




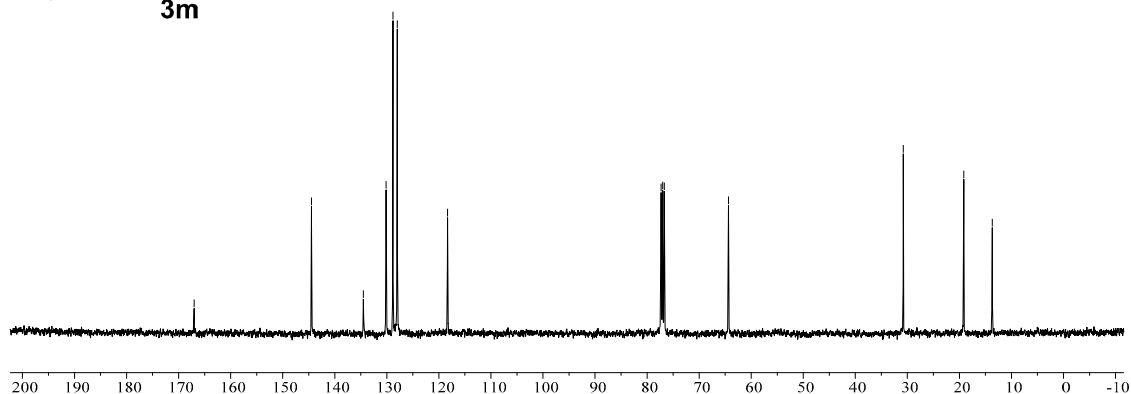
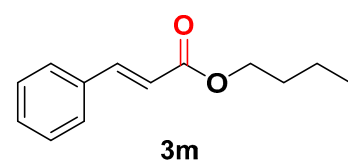
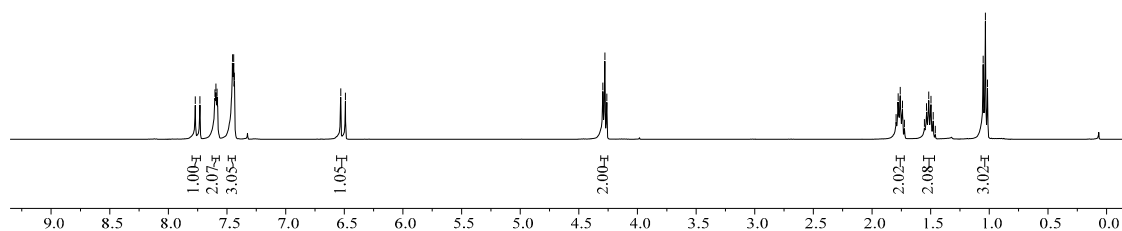
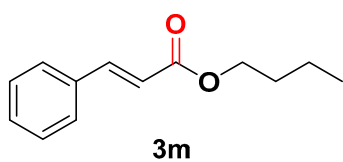
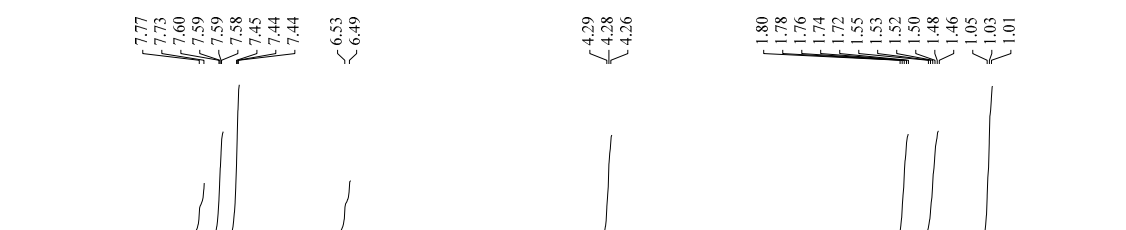


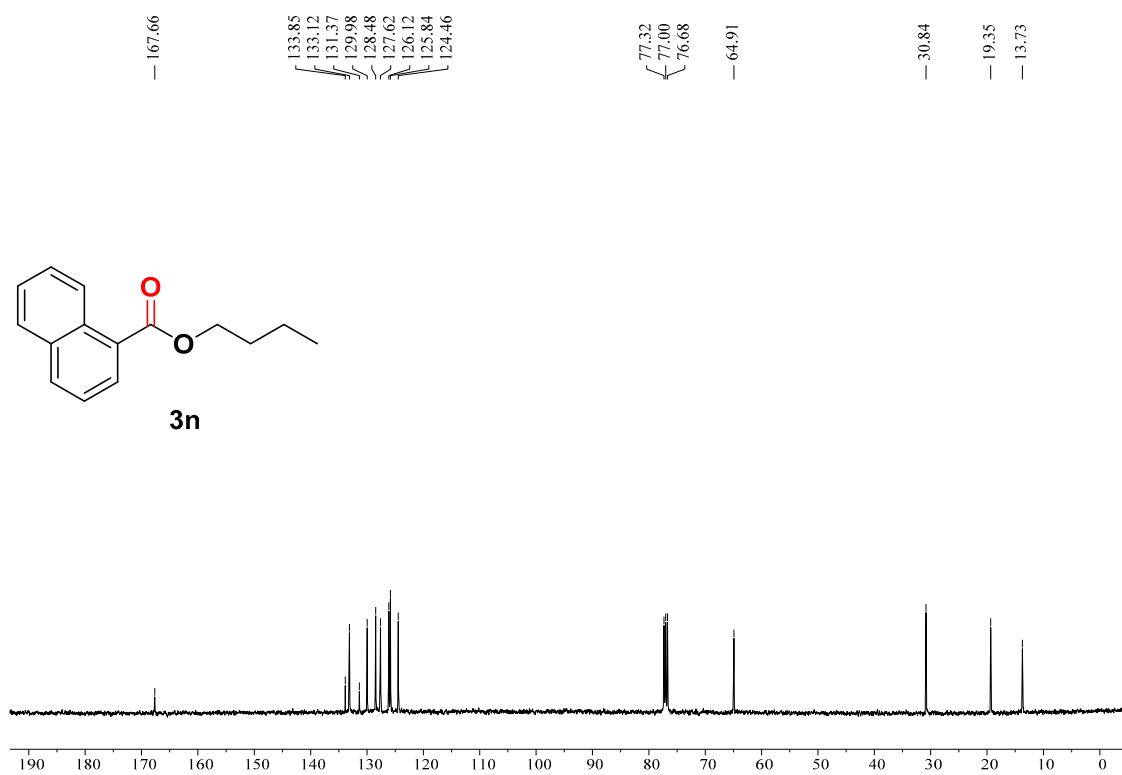
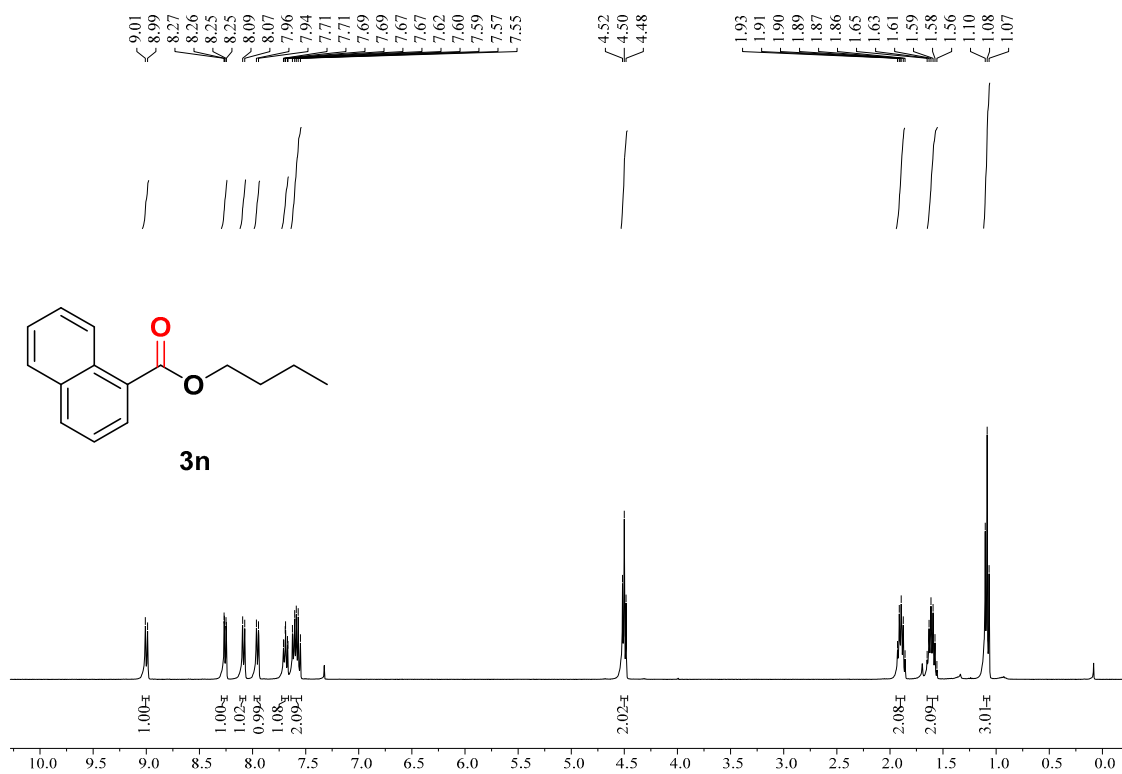


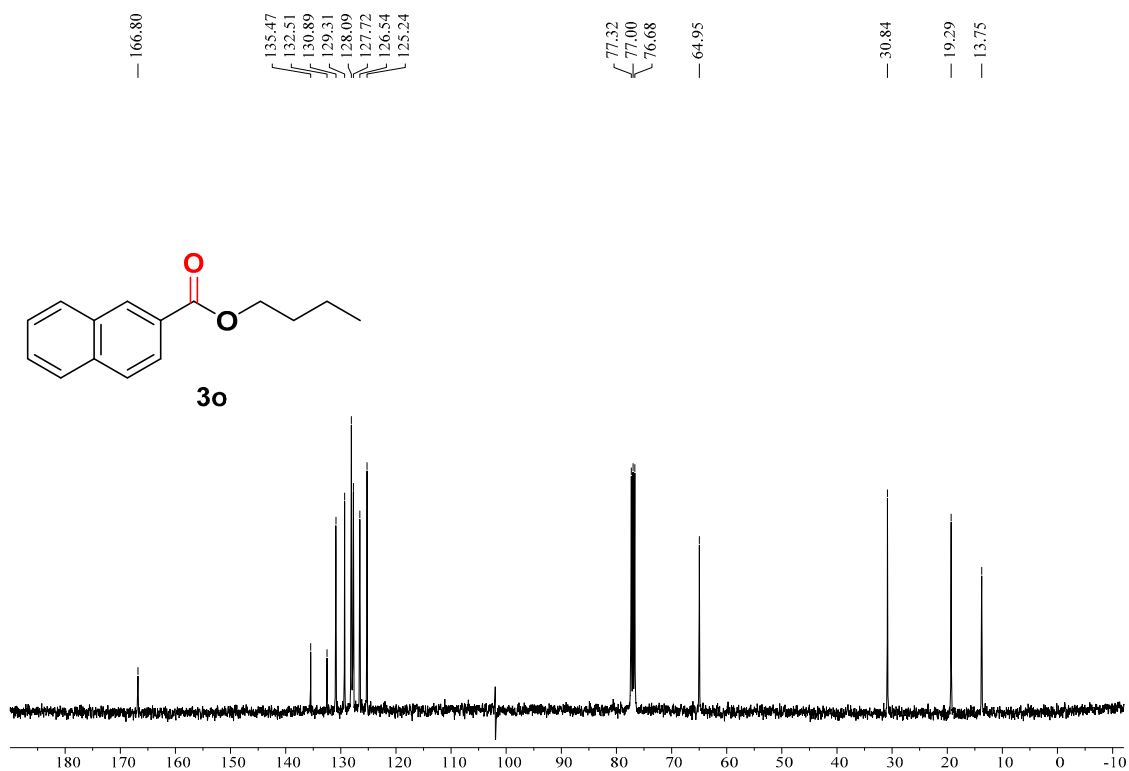
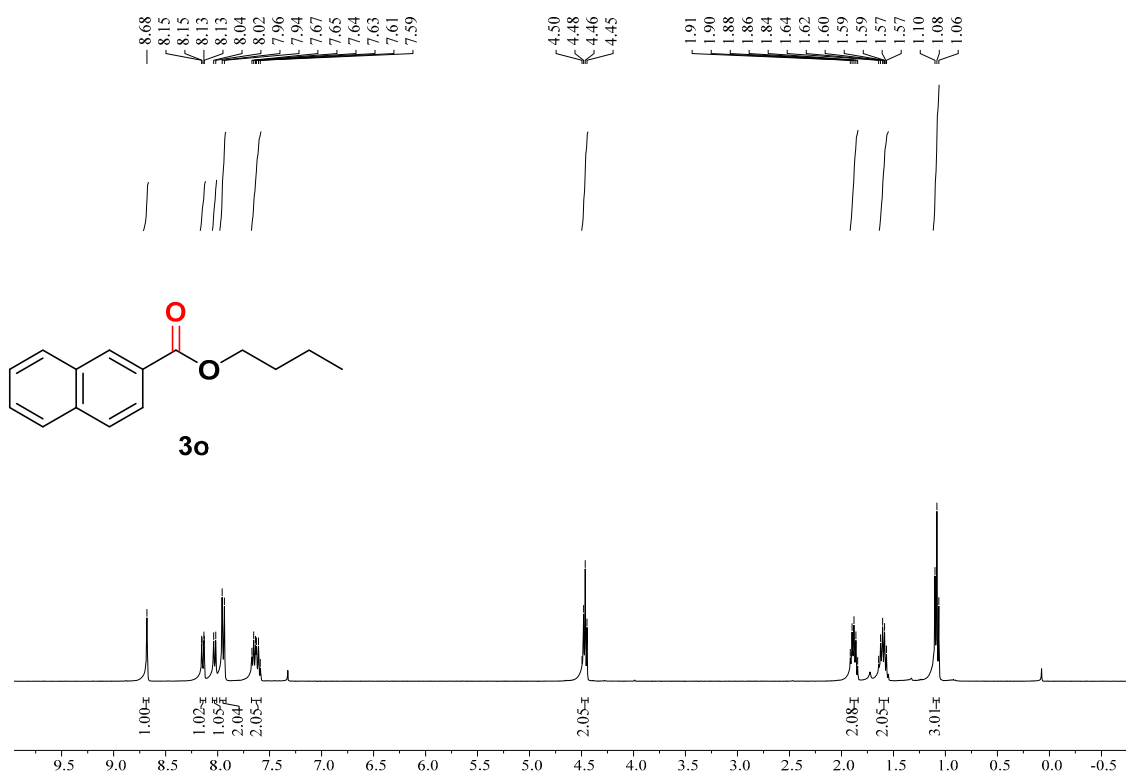


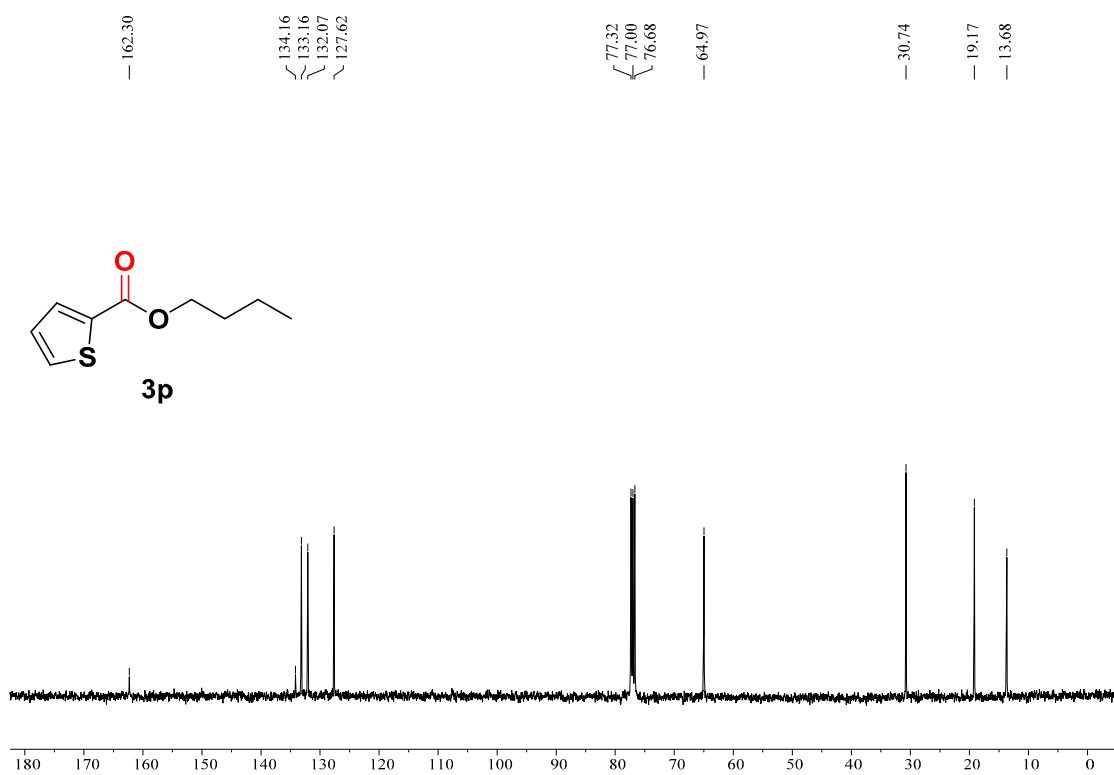
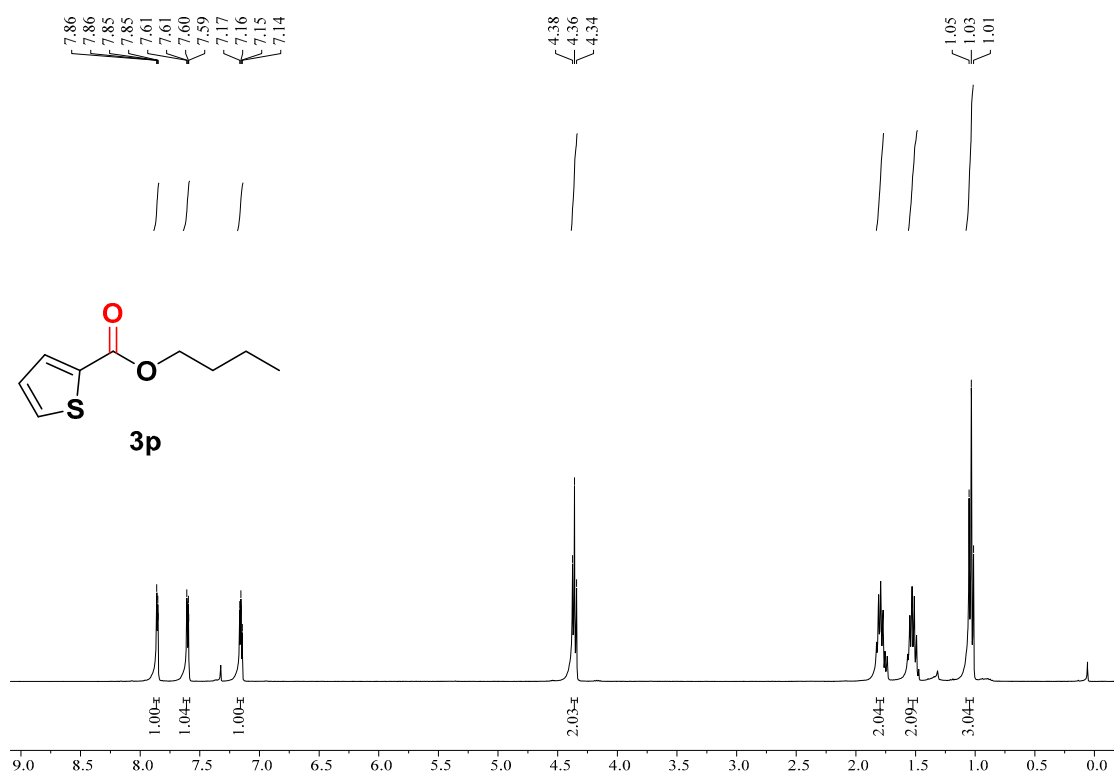


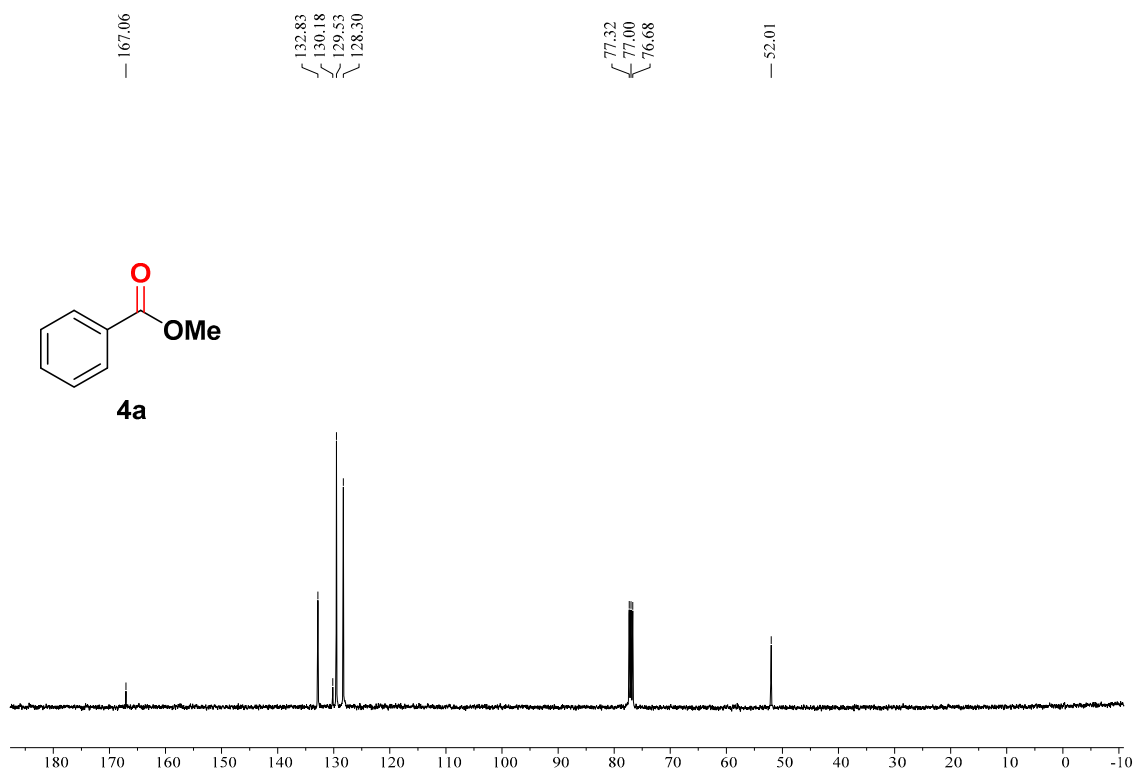
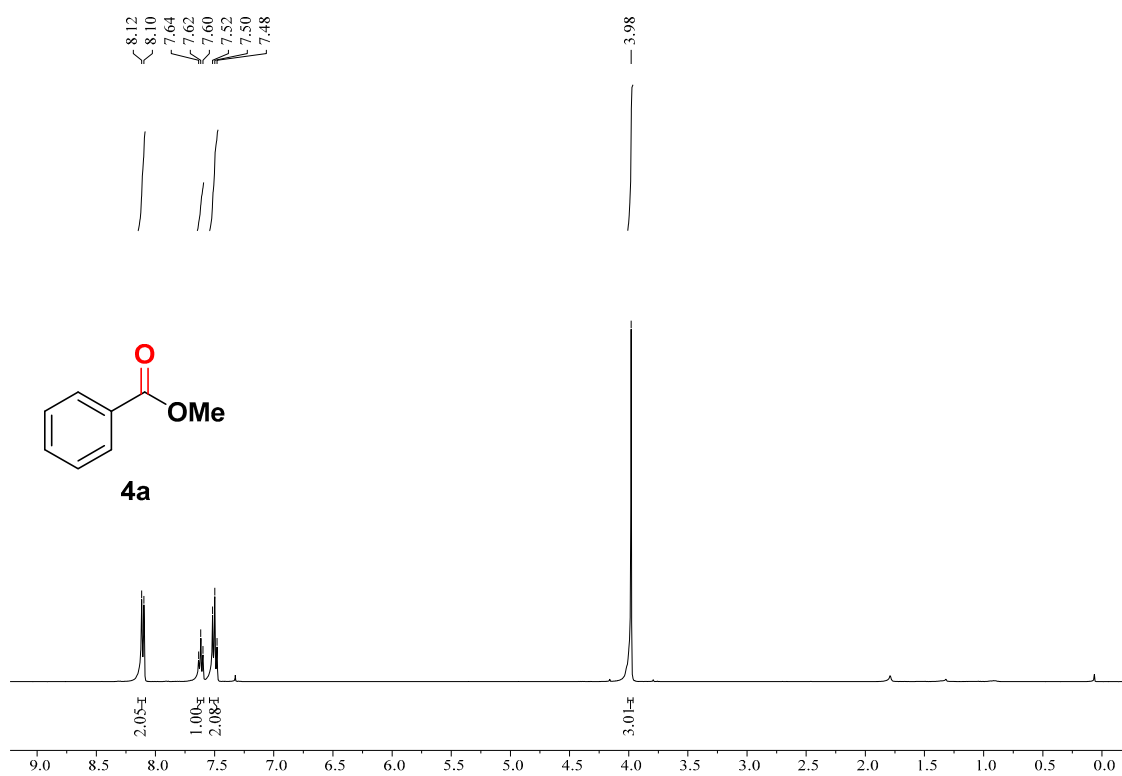


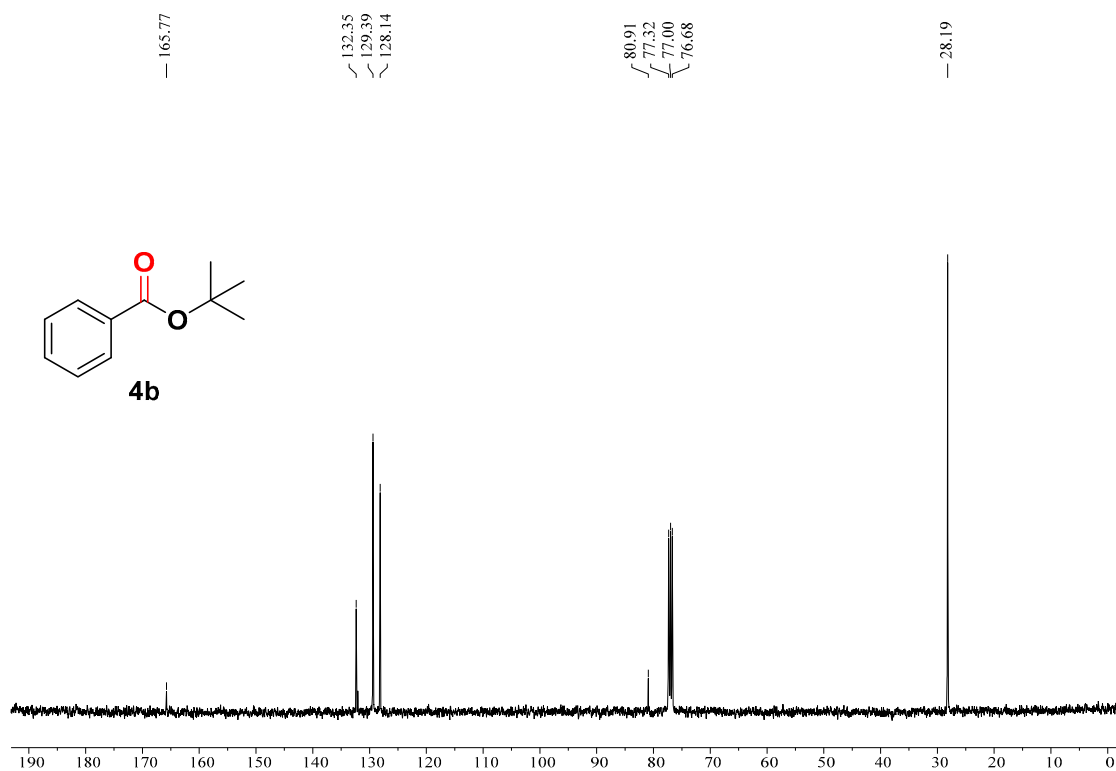
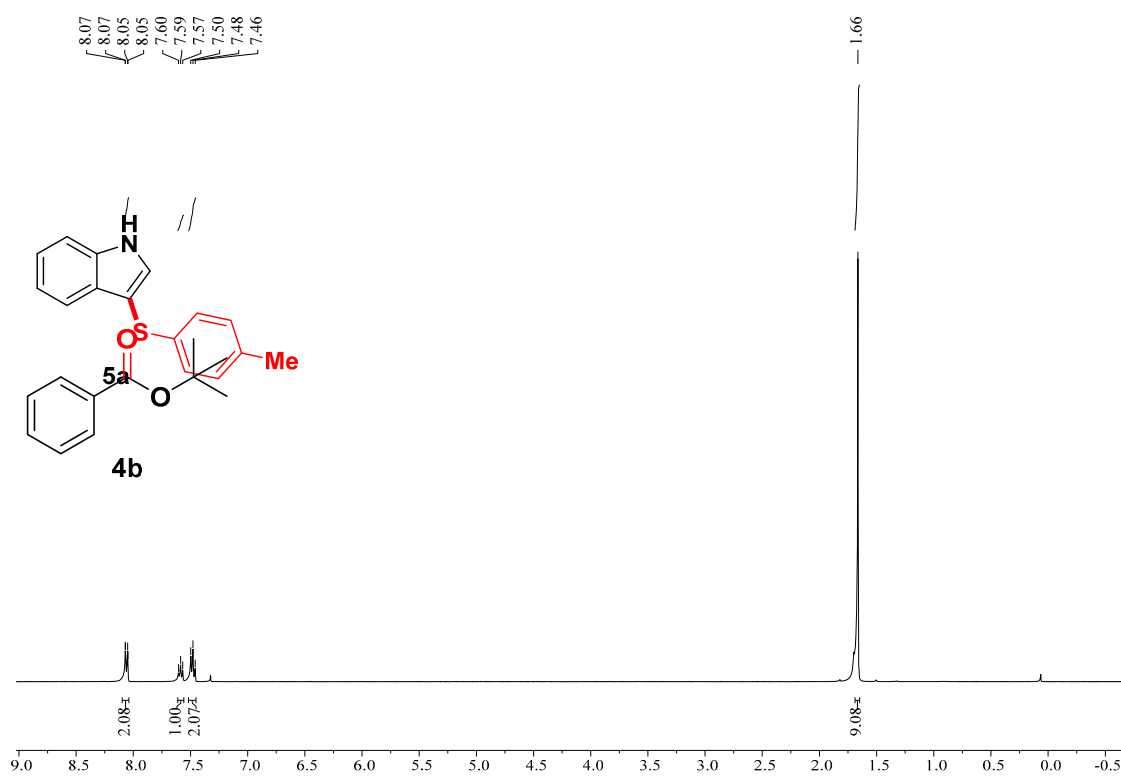


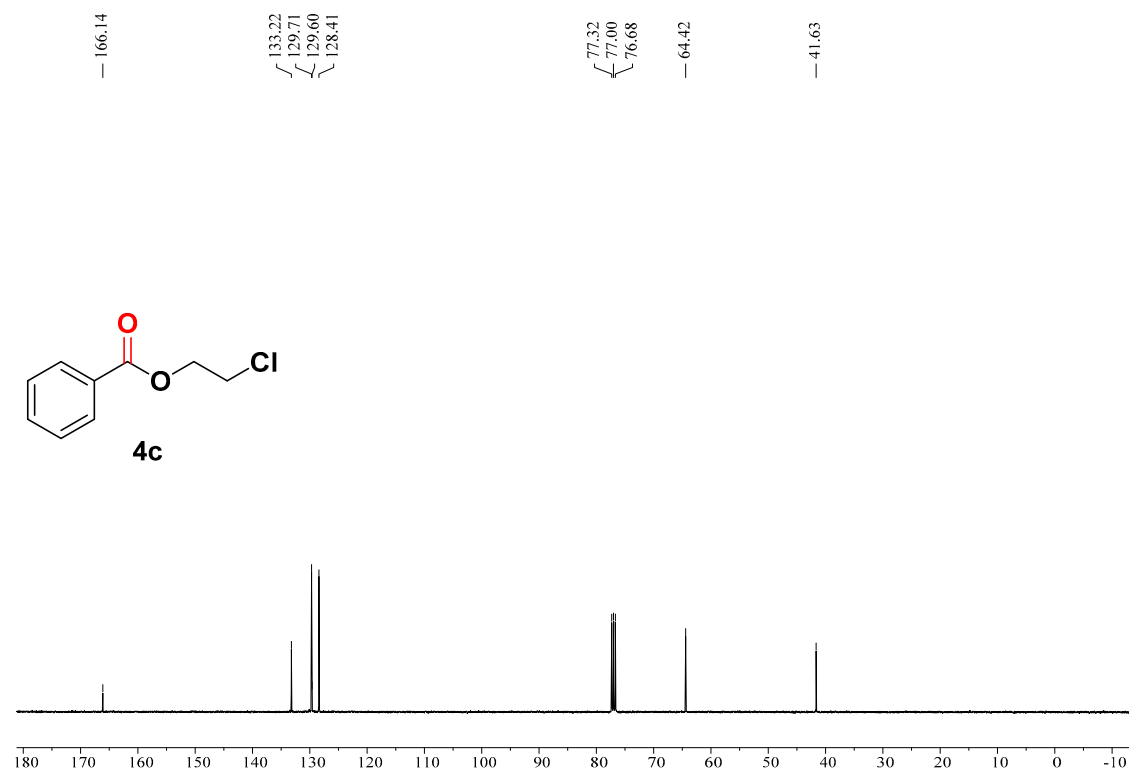
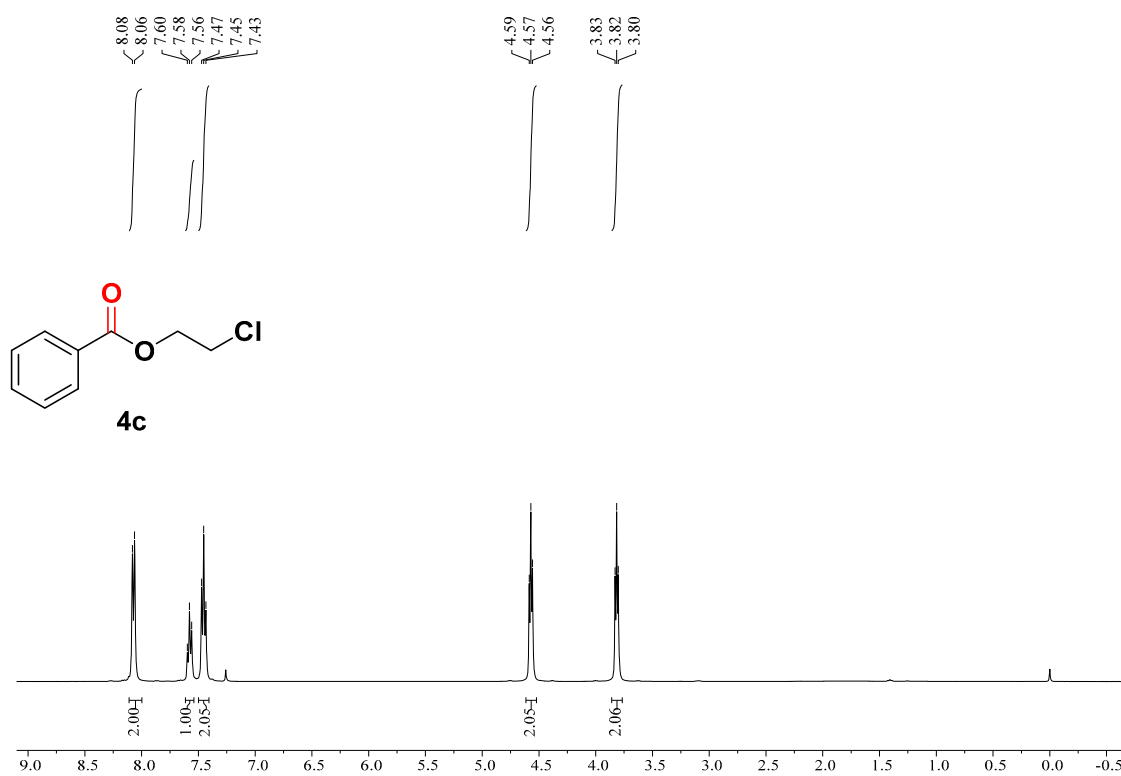


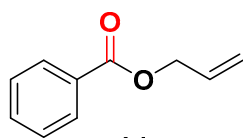
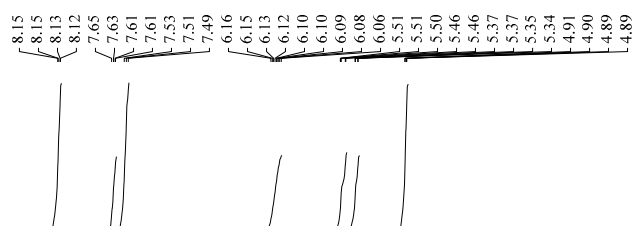




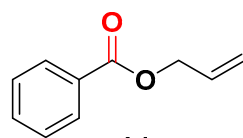
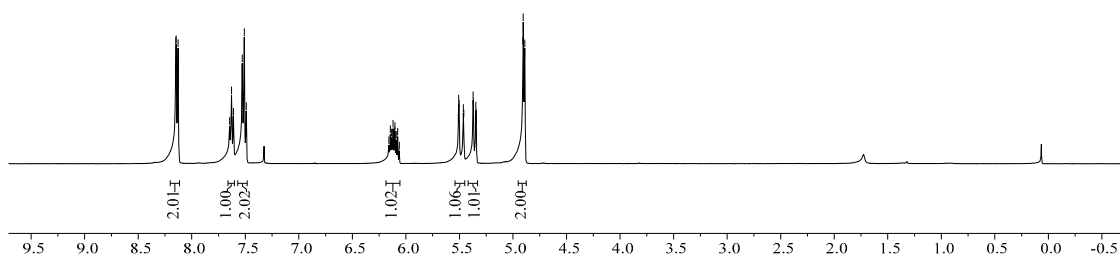








**4d**



**4d**

